Solid-state physicists and metallurgy

If they can tolerate apparent disorder and lack of cut-and-dried questions, solid staters should enjoy studying the practical properties of metals.

Roland W. Schmitt

Are there good problems for solid-state physicists in metallurgy? I believe so, both from the physicist's and the metallurgist's point of view. On the one hand are the important unresolved scientific questions, and on the other are industry's needs for special materials. A brief survey of the ways physicists can help those who study the uses of metals will show an underlying theme. Metallurgists need theories that can help them generalize from diverse experimental data without depending on detailed quantum-mechanical models; they need phenomenological theories.

High-strength materials

Why some materials are strong is one of the most fundamental scientific questions in metallurgy as well as one of the most important practical ones. High strength always leads us to a very basic quandary; as we go to materials of higher and higher strength, we find greater and greater brittleness. We understand qualitatively that to get strength (as in hardened steels), you must pin down dislocations, and to get ductility (as in copper) the dislocations must move.

Dislocation theory has been moderately successful as "enlightened empiricism," in Bruce ·Chalmers's phrase.[1] But dislocation theory has its limits. The stretch all the way from fundamental dislocation theory, which consists of crystal plane defects, dislocation generators and pinning sites, to an explantation of real experimental data, such as tensile-strength curves or stress–rupture curves, is usually long and awkward.

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Julian Schwinger commented on a situation analogous to this in his article: "An Engineering Approach to Particle Theory."[2] He said "Fundamental theory is too complicated, generally remote from the phenomena that you want to describe. Instead there is always an intermediate theory, a phenomenological theory which is designed to deal directly with the phenomenon. . . . The true role of fundamental theory is not to confront the raw data but to explain the relatively few parameters of the phenomenological theory in terms of which the great mass of raw data has been organized."

When metallurgists talk about stress–strain curves, stress–rupture curves, tensile strengths, yield strengths and so on, they are using phenomenological language. But it is an empirical phenomenology and does not link the data with fundamental theory. Almost every experimental investigation of strength yields a new set of special results. These results are interpreted in terms of dislocation mechanisms that are equally specialized and not generalizable. We need new phenomenologies in the spirit of Schwinger's remarks.

An example, taken from the work of Edward Hart at our General Electric Research and Development Center laboratory, shows the kind of theory that Schwinger was asking for.[3,4] Hart is studying plastic flow in polycrystalline materials. The basic variables for plastic deformation are stress, σ, strain ϵ, strain rate $\dot{\epsilon}$ and temperature T. Hart writes an empirical equation relating differential changes in these variables along any path in the space of the variables

$$d\ln \sigma = \gamma\, d\epsilon + \nu d\ln \dot{\epsilon} + Q d(1/kT)$$

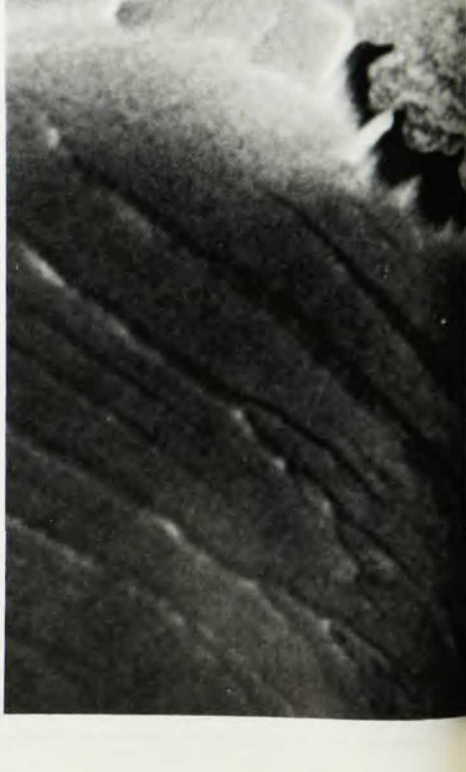
where γ, ν and Q are coefficients. You may sense that the style of this equation is that of a physicist, not a metallurgist. Next, he argues that for the class of materials and processes he is dealing with, stress, strain rate and temperature are good state variables.

$$\gamma = \gamma(\sigma,\dot{\epsilon},T)$$

$$\nu = \nu(\sigma,\dot{\epsilon},T)$$

$$Q = Q(\sigma,\dot{\epsilon},T)$$

Hart then shows that if the coefficients γ, ν and Q are functions of the state variables only, and if ν and Q are approximately constant, then $\gamma d\epsilon$ is a perfect differential, $\gamma d\epsilon = d\ln Y$. Y



turns out to be a measure of hardness. The result of all this reasoning is that an equation of state of plastically deformable systems is possible:

$$\sigma = Y\dot{\epsilon}^{\nu}e^{Q/kT}$$

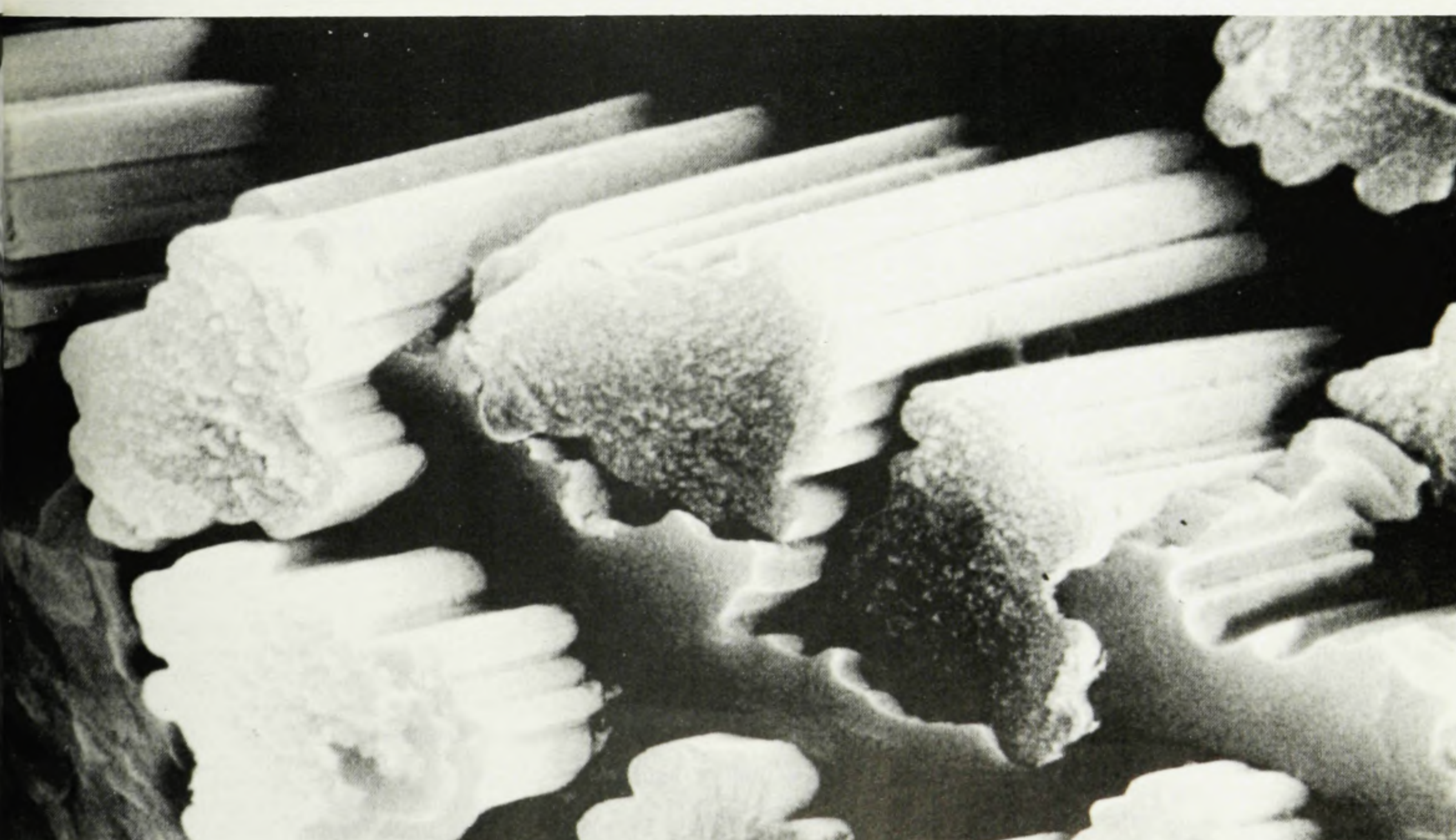
This equation would be a long-sought goal of the study of these systems. If, as appears likely from the few cases where suitable data are available, Hart's proposal is valid, scientists concerned with the plastic properties of metals should have a very much improved way to relate the empirical world of data to the microscopic world of dislocations.

Composites

Fiber-reinforced composites are becoming an important class of high-strength materials (see figure 1). These composites are basically fibers of a strong, but perhaps brittle, material embedded in a matrix of a weaker, ductile material. The fibers may be aligned to produce composites with highly anisotropic properties. A great many kinds of fibers have been studied, such as fine metal wires, glass fibers, crystalline whiskers, boron coating on fine tungsten wire, carbon filaments and polycrystalline ceramic fibers. Plastics or metals are used for the matrices.

Composites can take advantage of both the high strength of fibers—even the brittle ones—and the ductility of the matrix, so that the trade-off between strength and ductility is radically altered. The result can be a very strong and yet comparatively light material.

Carbon fiber in an epoxy matrix. Fiber-reinforced composites combine high strength and ductility. The usual problems of analyzing material strength are complicated by inhomogeneity.
Figure 1



Crack in a high-temperature alloy. Growth of cracks such as this one causes metal fatigue. Scanning electron micrograph shows the surrounding oxide growth that accelerates the fatigue process. Figure 2

Composites, already important in aerospace construction, will probably soon be in widespread use.

Although many problems related to composites are chemical in nature, a few physicists should look at this field. All the normal problems of material strength are going to be more difficult in these materials, because they are inhomogeneous. Dislocation theory will be limited in its usefulness. And neither long experience (which we do not have) nor traditional engineering approaches are going to be adequate. New phenomenological theories will be needed, and the training and intellectual habits of physicists are best suited for this approach.

Radiation-tolerant materials

I include radiation-tolerant materials mainly because of the intense need for them in the nuclear industries. But there are also significant scientific questions. We understand quite a bit about elementary forms of radiation damage in simple materials, and research into this kind of damage is still active and fruitful. But in nuclear reactors, we have complex materials, for example, ceramic fuel pellets, alloyed zirconium or steel cladding and other steels in structural elements. These materials are subjected to massive doses of complex radiation during the entire lifetime of the reactor.

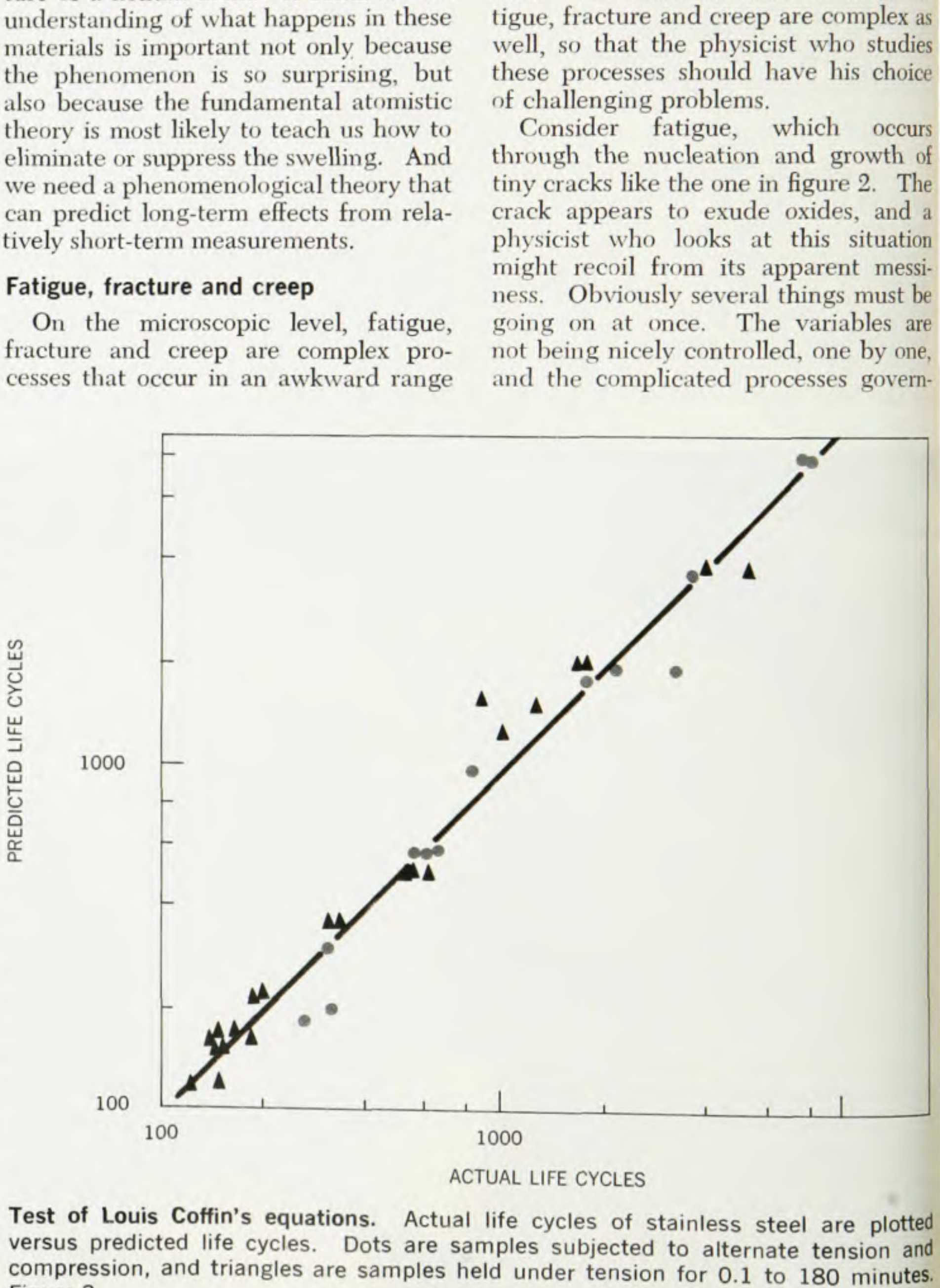
Fast-neutron damage of stainless steel provides an example of the possible complexities. In 1966 some metallurgists at the Atomic Energy Research Establishment, Harwell, UK, noticed that pieces of stainless steel that had been exposed to fast neutrons for a long time would swell. When they examined the pieces of steel with an electron microscope, they saw that the swollen pieces were filled with pores. But these pores, surprisingly, were not filled with gas; the pores disappeared entirely when the samples were annealed at high temperatures.

Vacancies produced by energetic neutrons apparently cluster into small pores, which are probably stabilized by capture of a helium atom. A fundamental understanding of what happens in these materials is important not only because the phenomenon is so surprising, but also because the fundamental atomistic theory is most likely to teach us how to eliminate or suppress the swelling. And we need a phenomenological theory that can predict long-term effects from relatively short-term measurements.

Fatigue, fracture and creep

On the microscopic level, fatigue, fracture and creep are complex processes that occur in an awkward range of the size scale; they are too extensive to be considered atomic processes but too small for a continuum approximation. The materials used to resist fatigue, fracture and creep are complex as well, so that the physicist who studies these processes should have his choice of challenging problems.

Consider fatigue, which occurs through the nucleation and growth of tiny cracks like the one in figure 2. The crack appears to exude oxides, and a physicist who looks at this situation might recoil from its apparent messiness. Obviously several things must be going on at once. The variables are not being nicely controlled, one by one, and the complicated processes govern-



Test of Louis Coffin's equations. Actual life cycles of stainless steel are plotted versus predicted life cycles. Dots are samples subjected to alternate tension and compression, and triangles are samples held under tension for 0.1 to 180 minutes. Figure 3

Corrosion in a nickel–tungsten eutectic alloy is shown here in a photomicrograph at about 750× magnification. Surface phases are mixed nickel and tungsten oxides. Figure 4

ing the growth of each little crack probably differ from crack to crack. The eventual failure of the material must be a chancy event.

Despite the apparent complexities of the processes, several good empirical laws describing fatigue-induced failure have been developed. Louis Coffin (GE) has used the amplitude and the frequency-of-application of cyclical strains as variables in his rather simple equations. Figure 3 compares the measured lifetime of a type of stainless steel with that predicted by Coffin's equations. We see that there is a great regularity of behavior here that can be extracted empirically; this regularity defies the impression of uncontrolled complexity seen by the solid-state physicist oriented toward fundamentals.

Oxidation and corrosion

Oxidation and corrosion (see figure 4) often limit the use of otherwise valuable materials. These problems have more to do with chemistry than with solid-state physics, but surface physics is directly pertinent. We shall discuss stress–corrosion cracking to get some idea of the physics of oxidation and corrosion.

Stress–corrosion cracking is a type of fracture that takes place only when stress and a corrosive environment are simultaneously present. It occurs in materials of great practical importance, for example, in stainless steels and in titanium alloys. Stress–corrosion cracking does not occur in pure metals and appears to involve electrochemically induced propagation of a crack through a material.

The phenomenon is one to which fundamental theories of physics can contribute; Robert Schrieffer, the superconductivity theorist, has written a paper with W. A. Tiller on stress–corrosion cracking.[5] Schrieffer and Tiller show that the stress field around a tiny crack in a metal causes a redistribution of the free electrons in the metal. This redistribution can affect the surface potentials in the crack, leading to stress corrosion.

Superconducting materials

Metallurgists have really begun studying superconductivity only during the last decade, with the discovery of high-field superconductors. Physics led metallurgy into this area, and it has been one of the most fruitful for interactions between the two disciplines. Superconductivity has a rich history of phenomenological as well as fundamental theories. Bernd Matthias, for example, uses a set of more or less empirical rules that guide him in his search for superconductors with higher and higher critical temperatures.

The critical-state model[6,7] is a good example of the way a theory can affect a discipline. This model was introduced to help understand the magnetization curves of high-field superconductors. In its simplest form, the model assumes that a changing flux density in a high-field superconductor induces persistent currents, up to a limiting, or critical, current density. This rather simple phenomenological assumption was sufficient for an understanding of the magnetic fields, and it was also very quickly applied to alternating-current losses.

Shortly after its introduction, the critical-state model began to be related to a more physical picture of magnetization behavior, through flux–flow[8,9] and flux–creep[10] theories. These theories assume that flux filaments move through the materials subject only to mutual repulsions, viscous drag and attractive interactions (pinning) by defects.

This hierarchy of theories and concepts has given high-field superconductivity its vitality during the last few years, and has encouraged interaction between physicists and metallurgists, and physicists and coil designers (see figure 5). It has also given us the ability to think about and deal with complex materials and configurations.

At this point an analogy with plastic deformation is useful. I think that Hart's concepts, which I described earlier, bear a striking relationship to the concepts of the critical-state model, and that the opportunities for physicists in plastic deformation will be similar to the opportunities in high-field superconductors.

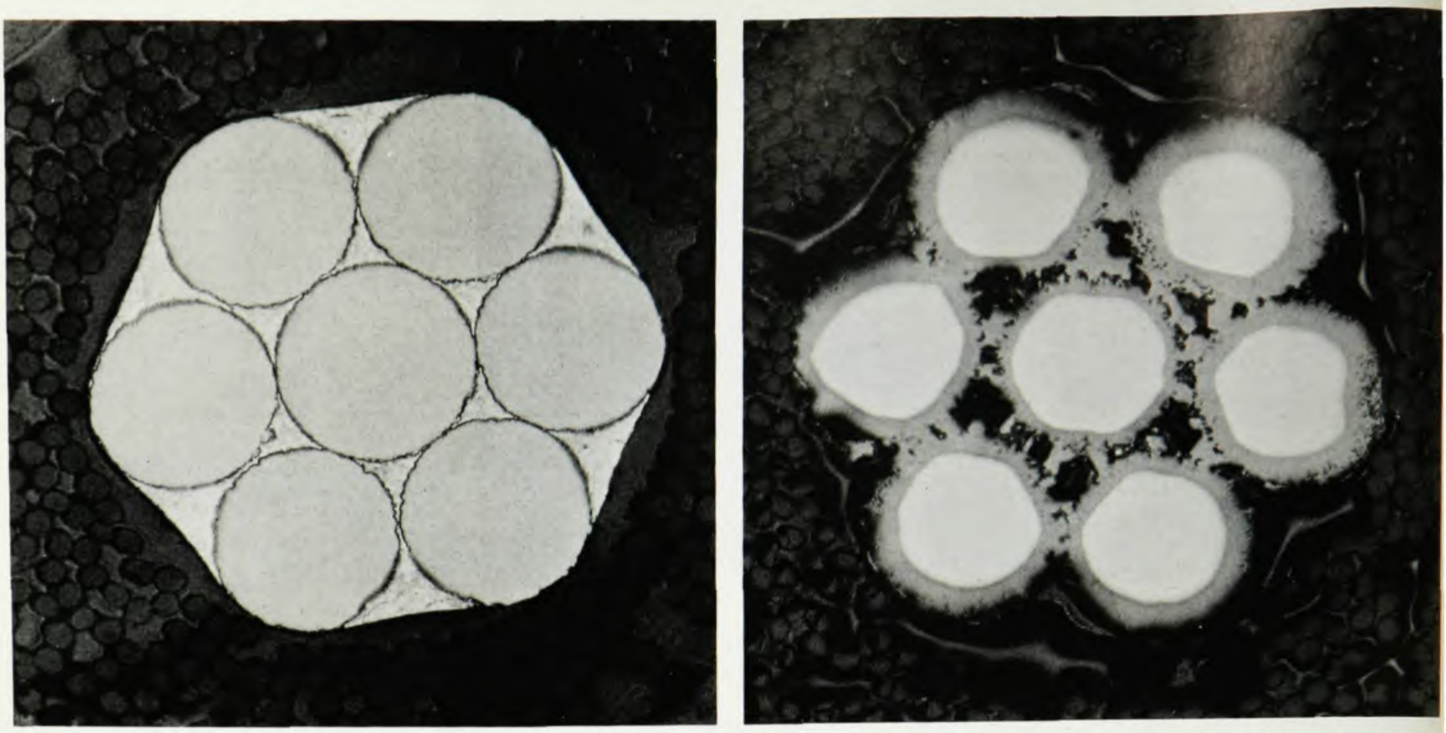
Solid electrolytes

Ceramic, glassy or crystalline materials sometimes have very high ionic conductivity, comparable to a highly conducting aqueous electrolyte. If these solid electrolytes have no accompanying electronic conductivity, they can be used in batteries, fuel cells and other devices dependent on ionic conduction.

From the viewpoint of potential applications, the most interesting new solid electrolytes are those with the so-called β-alumina crystal structure. Sodium β-alumina (sodium aluminate), the best known of these compounds, has a crystal structure in which all of the sodium atoms appear in layered planes. Other ions can be substituted for the sodium ions; one of the potentially more useful ones is the hydronium ion H_3O^+.

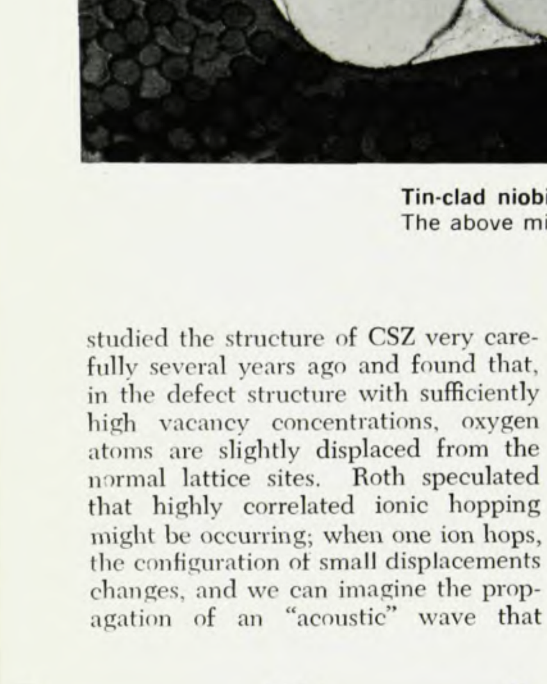
A better understood compound is calcia-stabilized zirconia (CSZ), a solid electrolyte that has been studied at GE (see figure 6). It has a cubic structure formed from about 15 mole per cent calcium oxide in zirconium dioxide. Wherever a calcium ion replaces a zirconium ion, an oxygen-ion vacancy must also appear, to compensate for charge, so that the concentration of vacancies in the crystal can be very high, sometimes 10 to 20%. The electrical conductivity of the material is so high that the normal conductivity mechanism, individual ions hopping from occupied to vacant lattice sites, can not easily account for it. And the conductivity varies with about the seventh power of the vacancy concentration!

Ralph Carter and Walter Roth[11]



Tin-clad niobium cable (left) becomes Nb_3Sn superconducting wire (right) when treated with heat. The above micrographs, at about 300× magnification, are cross-sectional views. Figure 5

studied the structure of CSZ very carefully several years ago and found that, in the defect structure with sufficiently high vacancy concentrations, oxygen atoms are slightly displaced from the normal lattice sites. Roth speculated that highly correlated ionic hopping might be occurring; when one ion hops, the configuration of small displacements changes, and we can imagine the propagation of an "acoustic" wave that causes nearby ions to hop.



Calcia-stabilized zirconium oxide. Its unusually high conductivity led to a new theory of ionic transport. Figure 6

Roth's explanation is highly pictorial and intuitive. But recently, Michael Rice of our laboratory has worked out a proper theoretical treatment of collective modes of ionic transport. This kind of motion becomes possible when the number of vacancies is a significant fraction of the number of ions. His results reinforce Roth's hunch that cooperative ionic jumps might indeed account for the properties of CSZ. Here then, the materials scientists have opened some fascinating physics problems.

Metallurgy and biology

We have seen the common interests shared by solid-state physicists and metallurgists. There is also some resemblance between biology and metallurgy. The attribute that these two sciences share is the complexity of the materials, as well as of the phenomena and systems. In both metallurgy and biology, of course, a physicist can sometimes spot a pure-physics problem, a problem that he can carry intact to his own lab.

But the materials, phenomena and systems that are truly important in metallurgy or biology possess a complexity that can not be entirely neglected. The physicist who really wants to do the most important work in either of these disciplines must take the trouble to learn something about the field as it is perceived and described by those already in it, and he must develop a taste for working on problems with greater intrinsic complexity than the usual ones in physics. If the physicist who thinks he wants to work in biophysics has any doubts, he might try metallurgy first. In metallurgy he will discover whether or not he can tolerate complexity, but he need not simultaneously learn a large number of new scientific laws, principles and mechanisms, because metallurgy, unlike biology, shares these with physics.

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