# When Crystals Collide: Grain Boundary Images

*Internal interfaces in metals, ceramics and other materials strongly influence the properties of those substances. New work gives the best data to date on the atomic structure of such interfaces*

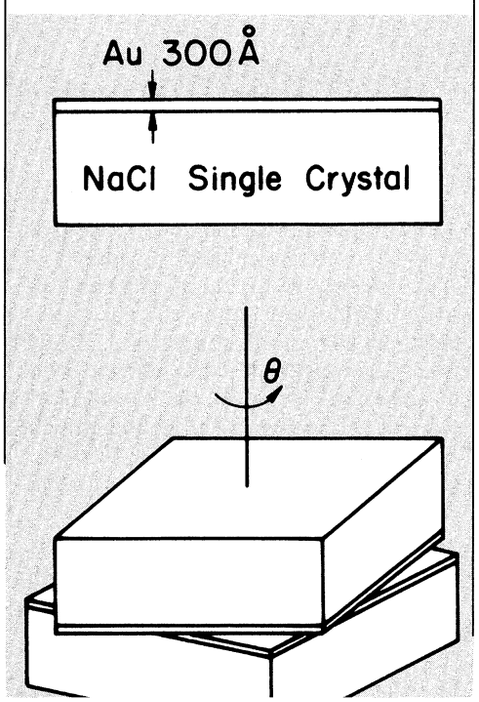
INTERESTING THINGS HAPPEN at boundaries, whether material or geographical. Granted, a piece of polycrystalline silicon and the Middle East have little in common, but if you don't mind stretching an analogy to its breaking point, you can see a parallel. Diplomats watch the Israel-Lebanon border to look for increased tensions or eye the Iran-Iraq border to see how the cease-fire is going. Materials scientists study grain boundaries—the internal interfaces between two separate regions of a crystalline substance—to understand better the properties of such materials as metals, ceramics, and minerals.

Recently, two researchers from Cornell University obtained the most detailed data ever on the positions of individual atoms along a boundary between two crystalline regions. The detailed picture that emerged from that data not only provided the most accurate information to date on the structure of a grain boundary, but it also allowed the two scientists to show that the arrangement of atoms along the boundary could be represented by a simple geometric model. Although the researchers so far have characterized only two very specialized grain boundaries, the work eventually may lead to general rules predicting the positions of atoms along all such boundaries. This improved understanding of the boundary structure could in turn lead to useful improvements in the properties of metals, ceramics, and other materials.

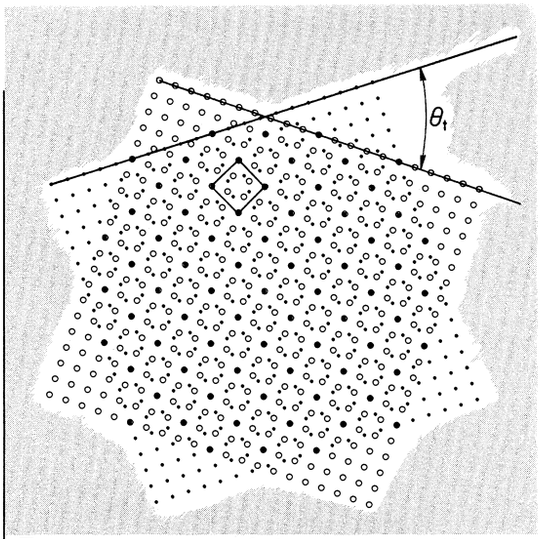
Many of mankind's most important materials have crystalline structures—ceramics, metals, and silicon-based semiconductors are some of the best known examples. The atoms of these materials line up in orderly rows much like a high school marching band at halftime of a football game, except of course that the materials are three dimensional while the pattern of the band is two dimensional. Metals and ceramics usually do not look crystalline—as does, say, a piece of quartz—because they are composed of many small single crystals joined together at interfaces called grain boundaries. It is like having several marching bands on the field at once, all of them aimed at different angles and jammed up against one another.

These grain boundaries often play a profound role in determining the properties of a polycrystalline material (one consisting of many crystalline grains). The mechanical properties of such a material, for instance, are determined in part by how grains slide past each other at their boundaries. The compound $Ni_3Al$ is very brittle in pure form, but increasing the nickel proportion slightly and adding a little boron makes it ductile—the boron moves to the grain boundaries where its presence makes the compound more malleable. On the other hand, pure iron is ductile, but adding an impurity such as sulfur or antimony at the grain boundaries makes it brittle.

To understand how the grain boundaries affect a material's properties, scientists need to understand the structure of the boundaries: How do the atoms position themselves in the transitional regions between one crystalline grain and the next? It is a difficult question because while the atoms in a single grain are arranged in simple, repetitive, easy-to-understand arrays, the atoms between grains can be distorted into many different configurations.




**A twist boundary in gold** *was formed by laying down a 300-angstrom thin gold crystal on a salt substrate, then hot pressing two such crystals together at an angle.*



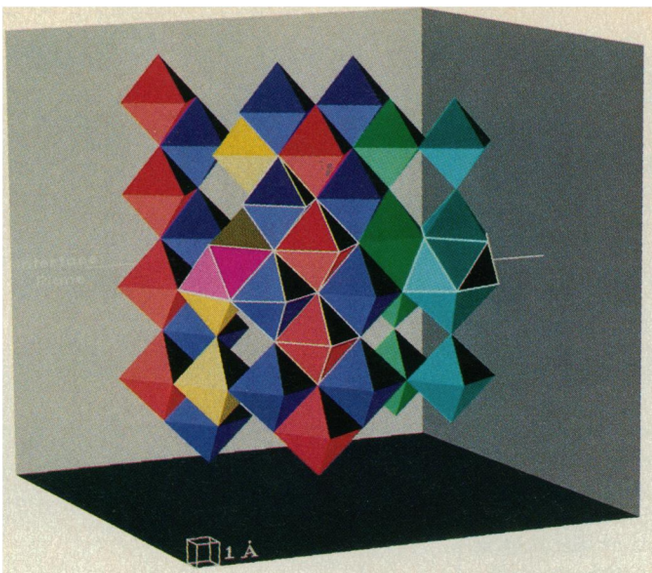

**Two square arrays of atoms** *meet at 36.9° and create a new repeating pattern.*

To simplify the problem, materials scientists look at two special types of grain boundaries: tilt and twist. A tilt boundary looks just as it sounds—think of two marching bands coming together at an angle. A twist boundary needs three dimensions for visualization—imagine two identical bands, one of them floating just over the heads of the other, and then rotate the top one. Most grain boundaries are a mixture of twist and tilt, but because these combinations are so complicated, researchers usually study one or the other in isolation.

Studying twist boundaries in gold, Stephen Sass and Michael Fitzsimmons at Cornell have used x-ray diffraction to map the positions of individual atoms in the boundaries to within an accuracy of 0.1 angstrom. The accuracy of their x-ray diffraction studies, which were done at the Cornell High Energy Synchrotron Source, was several times greater than that obtained in earlier work on grain boundaries done with electron microscopes, Sass says. The researchers describe their work in papers to be published in *Acta Metallurgica*.

X-ray diffraction is a standard method for determining the structure of crystals. A researcher aims an intense beam of x-rays at a crystal, and the atoms in the crystal scatter the x-rays in a pattern that depends on the particular arrangement of the atoms and the angle at which the beam hits the crystal. Analysis of the diffraction pattern—which looks like a pattern of dots of light of varying brightness—can reveal the crystal's structure.

It is not so easy with a grain boundary.

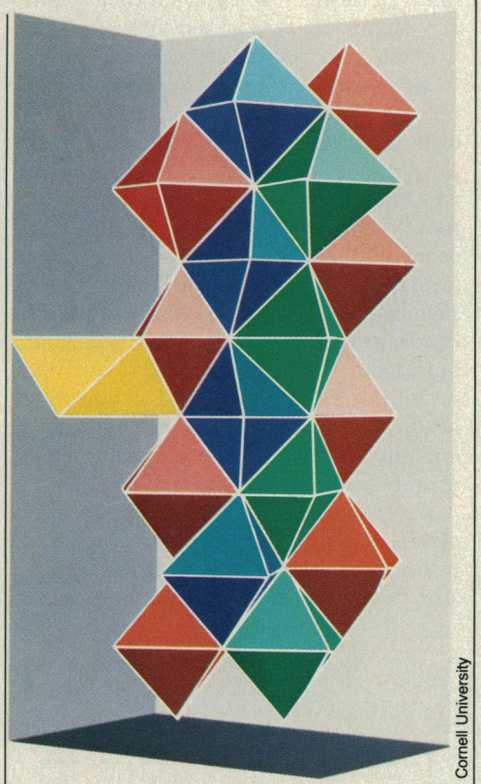



**Computer-generated pictures** *of columns of atoms in twist grain boundaries in gold, with a 22.6° twist angle above and 36.9° angle below. The gold atoms are located at the vertices of the individual polyhedra, and the effects of the twist can be seen in how the orientations of the octahedra change from the bottom of the picture to the top.*

For one thing, the arrangement of atoms along a boundary is much more complicated than in the body of the crystal, which means the diffraction pattern and the analysis of it are much more complex as well. Second, there are many fewer atoms in the boundary than in the body of the crystal, which means the diffraction pattern is much weaker. A third problem is that the body of the crystal contributes its own scattering points to the diffraction pattern, which can obscure information from the boundary.

To get the best diffraction pattern possible from the boundary, one wants a thin bicrystal with a large, clean grain boundary inside it. To create such a bicrystal, Sass and Fitzsimmons used a hot pressing technique invented in 1969 by Robert Balluffi of the Massachusetts Institute of Technology. Beginning with two flat crystals of salt, they evaporated a 300-angstrom layer of gold onto each. The salt crystals acted as templates so that the gold formed single crystals. These two crystals of gold were misoriented and then hot pressed together to make a single 600-angstrom-thick bicrystal, with a twist boundary in the middle. Afterward, the salt was dissolved, leaving the gold bicrystal free for study.

In simple crystals, the arrangement of the atoms can be determined from the diffraction pattern with a relatively simple analysis. The complexity of these grain boundaries made that impossible, so Sass and Fitzsimmons worked in the other direction. Starting with possible models of the boundary structure, they calculated what the diffraction patterns would look like for a given arrangement of atoms along the boundary and compared those patterns with the experimental patterns. They varied the positions of the atoms in the models until the diffraction patterns from the model agreed closely with those from experiment. The Cornell National Supercomputer Facility was used for the analysis.



Cornell University

For a boundary with a twist angle of 36.9°, the positions of the atoms in the grain boundary were determined to within 0.09 angstrom. (The atoms in a crystal of gold are spaced 2.88 angstroms apart.) For a twist boundary with misorientation of 22.6°, the two researchers made more diffraction observations, so they could determine the positions of the atoms in the boundary with even greater accuracy—to within 0.06 angstrom perpendicular to the interface and within 0.02 angstrom parallel to it.

Having mapped the positions of the atoms in the boundary, Fitzsimmons and Sass found a natural way to model them. Other researchers had suggested the structures of grain boundaries might be represented by polyhedra, but no one had determined the structures accurately enough to be sure this worked well. Sass was looking at pictures of the atoms in the grain boundaries with lines drawn between adjacent atoms, when he realized, "Gee there are polyhedra all over the place." A polyhedron is a geometric solid, such as a pyramid, whose faces are triangles or squares or other polygons. The Cornell work showed that the positions of the atoms in the grain boundaries could be visualized by picturing the space filled up by various polyhedra—mostly eight-faced octahedra and four-faced tetrahedra—and thinking of the atoms as lying at the vertices of these solids.

With this insight, Sass and Fitzsimmons made computer-generated pictures of the grain boundaries using these polyhedra. Two of those pictures appear on this page. To use these pictures to visualize the position of the atoms in the grain boundary, imagine a single gold atom at each vertex of each polyhedron. The octahedra, each having six vertices, look like two pyramids glued together at their bottoms. One can think of them as being outlined, or defined, by six adjacent gold atoms.

In the body of the crystals, away from the boundaries, the structure can also be modeled with octahedra and tetrahedra; indeed, this is a standard way to visualize the structure of a crystal. In the pictures on this page, one can see the twist of the boundary reflected in how the octahedra change orientation from the bottom of the picture to the top. If one, for instance, follows the red octahedra up the pictures, it is clear they have changed their orientation from bottom to top.

Sass points to at least two expected benefits from this work. One, it gives theorists very accurate data with which to compare their predictions for grain boundaries. The atomic arrangements that the Cornell researchers described "don't agree well with theory," Sass says, but theorists have not had really good information with which to make models. "Now theorists are getting better models since they have better information to match their models against."

Two, the researchers' modeling of the grain boundary by polyhedra may be a step toward a general set of rules describing the structures of boundaries. In the 1920s, Linus Pauling devised a set of rules to describe the crystalline structure of ionic solids, such as salt, in terms of various polyhedra. Sass says it eventually may be possible to find such a set of rules for the structure of grain boundaries. If so, scientists then may be able to predict the structures of new grain boundaries and understand their properties.

■ **ROBERT POOL**