

Single Crystals from Metal Solutions

centration of less than about 5 percent (the limit we had established by x-ray diffraction techniques) would produce some increase, depending on its concentration. but the increase would be nowhere near that expected if UPt_3 itself was a superconductor. (The BCS theory predicts an increase of about 150 percent.)

The whiskers we could gather at the time for the specific heat measurement amounted to only 20 milligrams, but, fortunately, we have developed techniques and equipment for measuring specific heats of very small samples. We spent nine days hovering over the refrigerator, and by Friday, September 30 the data definitely showed a sizable discontinuity. However, because of experimental difficulties below 0.3 kelvin, there remained a nagging uncertainty about its precise shape.

Such an important discovery deserved the best possible data, so we decided to repeat the heat capacity measurements, this time using annealed whiskers. (We had learned from susceptibility measurements in the helium-3 apparatus that annealed whiskers had much sharper superconducting transitions, and this increased sharpness would be reflected in the heat capacity curve.) Since we were running out of whiskers, we took the unannealed ones out of the refrigerator, annealed them, and had them cold again by Monday, October 3. That weekend turnaround was the fastest we had ever achieved.

As shown in Fig. 3, the specific heat of our annealed single crystals of UPt_3 increased by only about 50 percent, and the transition was quite broad (and had been even broader for the unannealed crystals). Nevertheless, an increase of this magnitude unequivocally ruled out the possibility that the superconductivity was due to a minor second phase. We now felt confident that superconductivity and enhanced spin fluctuations coexisted in UPt_3 .

During these experiments we had repeatedly attempted to produce better samples and had significantly increased the size of the crystals but not their lattice perfection. In

Given a free choice, any solid-state experimentalist would characterize a material by making measurements on a single crystal rather than a polycrystalline sample. A single crystal more accurately represents the material (since it is free of grain boundaries at which impurities can hide) and is in fact required for measuring the directional dependence of various properties. Yet growing a single crystal can be exceptionally difficult, and a large number of important experiments await the preparation of appropriate single crystals.

Numerous techniques exist for growing crystals, but finding one that works for a particular material can be frustrating and time-consuming. A method we use quite often in our research is growth from slowly cooled solutions of the desired material in a molten metallic solvent, (This method is an easy extension of the observed natural growth of single crystals from aqueous solutions.) We have used as solvents such metals as aluminum, iridium, tin, copper, bismuth, and gallium. The solvent provides a clean environment for crystal growth, and the relatively low temperature at which growth occurs often results in low defect concentrations. Offsetting these advantages is the possibility that solvent atoms may appear at lattice sites and in voids of the crystal. In addition, one must find a container that is not attacked by any component of the solution and a chemical to remove the solvent without attacking the crystal. We have built up a collection of workable "recipes" and are constantly including new "ingredients." Still, success demands a certain flair.

When applying this technique to a new material, one unknown is always present: the material may be one that nature simply refuses to provide as nice crystals. Also, the appropriate phase diagram is usually lacking. Then we must rely on educated guesses and hunches, since determining the phase diagram for a system of at least three elements is not a job to undertake merely for exploratory work on crystal growth.

To grow the single crystals of UPt_3 , we used bismuth (melting point: 280 degrees Celsius) as the solvent. As usual, the phase diagram for the system was not available. But we knew from published work that UPt_3 has a melting point of 1700 degrees Celsius and is chemically quite stable, that reasonably large amounts of uranium and platinum can be dissolved in bismuth at temperatures on the order of 1000 degrees Celsius, and that compounds of both uranium and platinum with bismuth exist. But the shapes of the uranium-bismuth and platinum-bismuth phase diagrams indicated that these compounds are not exceptionally stable. Our guess—that UPt_3 would crystallize preferentially—was correct, provided that the solution was not cooled below about 1100 degrees Celsius (where a competing crystallization takes place). We obtained good yields by using atomic percentages of uranium, platinum, and bismuth in the ratio of 1:3:4 and an initial temperature of 1450 degrees Celsius. Since that temperature is near the boiling point of bismuth, we sealed the crucible in a tantalum can to prevent its evaporation. We used a crucible of BeO rather than the more usual Al_2O_3 because uranium might attack Al_2O_3 at such a high temperature.

As we improved the technique, we obtained crystals of UPt_3 with a length of up to 1 centimeter and a cross section of 1 millimeter by 1 millimeter. Nature shows her hand here. The material seems always to have a needle-like habit. ■