Fig. 7. Idealized specific heat curve for a superconductor with $T_c \approx 4.0$ K. A significant jump occurs at T_c. In the absence of a superconducting transition, the specific heat curve follows the dashed line and intercepts the ordinate at γ Near absolute zero, the lattice contributions go to zero rapidly, and the specific heat is due almost entirely to the electrons.

Fig. 8. Measured values of the specific heat for the $Y_{.10}Ir_{.90}$ system. Compare these measurements with the idealized curve in Fig. 7.

Importance of γ and β

Obviously, certain properties of materials in their normal state must lead to the electrons' overcoming their repulsive Coulomb interaction to form Cooper pairs and create the energy gap Δ at the superconducting transition. The purely theoretical considerations have been studied extensively and all known normal-state properties of various superconductors have been compared systematically. As a result, workers in the field are beginning to understand which properties are important for the superconducting state. The parameters γ and β determined by low-temperature specific heat measurement are found to be very important.

The parameter γ is proportional to N(0), the number of electrons at the most highly populated energy level (the Fermi level) in the normal-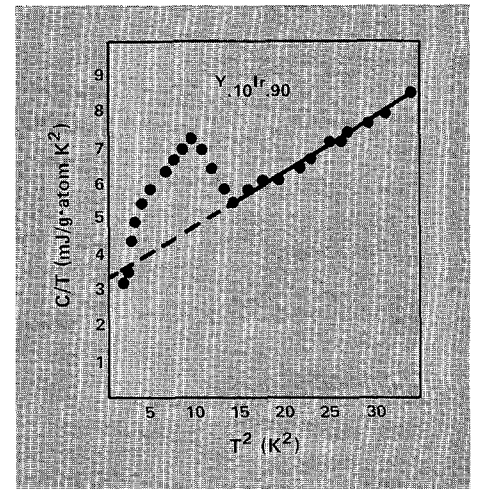state material, and to $(1 + \lambda)$, which depends on how strongly the material's electrons are tied to its lattice; it is given by

$$\gamma = \text{const.} \times N(0) \times (1 + \lambda). \qquad (5)$$

The parameter β is a measure of how stiffly the ions are held in place in the lattice by the material's electronic forces; it is given by

$$\beta = \text{const.}/\theta_D^3, \qquad (6)$$

where θ_D is the characteristic Debye temperature. The term θ_D was first introduced in a model of lattice vibrations proposed by Debye in 1912. The model describes the motion of the lattice ions by a superposition of quantized elastic waves propagating through the lattice. The quanta of elastic waves are called *phonons*. The Debye temperature, which is related to the cut-off frequency, can be thought of as the temperature at which the lattice forces responsible for the lattice stiffness are too weak to hold the ions in their places. Thus lead, a soft material, has a low θ_D (108 K), whereas iron, a hard material, has a high θ_D (464 K).

In 1957 Bardeen, Cooper, and Schrieffer developed the BCS microscopic theory of superconductivity and succeeded in relating T_c to γ and β.

$$kT_c = 1.14\,\hbar <\omega> \exp\left[-1/N(0)V\right], \quad (7)$$

where $\hbar$ is Planck's constant, $<\omega>$ is some average of the lattice phonon frequency related to θ_D, $N(0)$ is the electronic density of states at the Fermi surface, and V is the electron phonon interaction parameter. On this basis it was assumed that materials with high $N(0)$ (high γ) and high θ_D (high β) would be high T_c materials.

Solution of the Y-Ir Mystery

Events leading to discovery of the source of the enhanced superconductivity in the Y-Ir system produced a number of false leads. They demonstrate why low-temperature specific heat and metallographic examinations are vital to any critical study of superconducting materials. We had long known that the addition of as little as 1 atomic per cent yttrium to iridium metal raises the inductive and resistive T_c from 0.1 K to over 3 K. More recent LASL-UC, La Jolla, studies showed that the behavior is similar when europium is substituted for the yttrium; that is, the addition of a very small amount of europium to iridium causes a dramatic increase in the T_c. This new result rekindled interest in both the Eu-Ir and Y-Ir systems. We chose the Y-Ir system for a complete study of this novel effect because of the apparent absence of significant second phase for compositions as rich in yttrium as 10 atomic per cent and the absence of superconductivity in YIr_2, above 0.3 K.

We remeasured Y-Ir compositions from $Y_{.01}Ir_{.99}$ to YIr_2 using the ac susceptibility method. The signal magnitude in these measurements first increased with increasing yttrium con-

centration, reaching a maximum value near the $Y_{.20}Ir_{.80}$ composition and then decreased, becoming zero at the YIr_2 composition. The same results had been obtained in the earlier investigation and no doubt led to the suggestion that the superconductivity is due to the presence of a hypothetical phase of approximate YIr_4 composition. To investigate this possibility, we took new x-ray diffraction patterns of powdered samples of the same compositions using a Debye-Scherrer x-ray technique. The x-ray results indicated that no diffraction lines corresponding to a second phase were present in compositions up to 10 atomic per cent yttrium. The materials have a single-phase cubic structure with a relatively constant lattice parameter $a_0 = 3.8395$ Å, where a_0 is the distance between lattice sites. This structure, which is identical to and slightly larger than pure iridium ($a_0 = 3.8389$ Å), indicates that at most 1 atomic per cent yttrium is absorbed into the iridium lattice. The location of the remaining yttrium (up to 9 atomic per cent) remained a mystery.

We measured the low-temperature specific heats of the samples to determine how much of each sample was superconducting. Actual measurements for the $Y_{.10}Ir_{.90}$ system are shown in Fig. 8. The size of the specific heat discontinuity at T_c indicated the following percentages.

Composition	Superconducting Phase (%)
$Y_{.01}Ir_{.99}$	8
$Y_{.025}Ir_{.90}$	20
$Y_{.10}Ir_{.975}$	56
$Y_{.17}Ir_{.83}$	70

These results are similar to the results observed in the ac susceptibility

measurements and indicate that the superconductivity is indeed due to a bulk superconductor whose concentration increases as the yttrium content increases. The low-temperature specific heat measurements also gave very valuable information on the parameters $N(0)$ and θ_D. As shown in Fig. 9, the value of γ, which is proportional to $N(0)$, remains almost unchanged through most of the range, while the value of θ_D, which is inversely proportional to β, undergoes an enormous reduction.
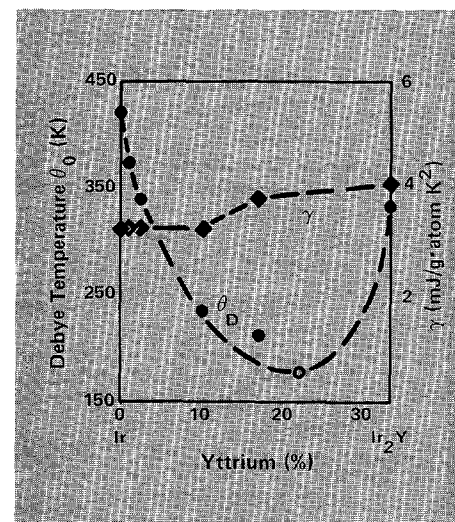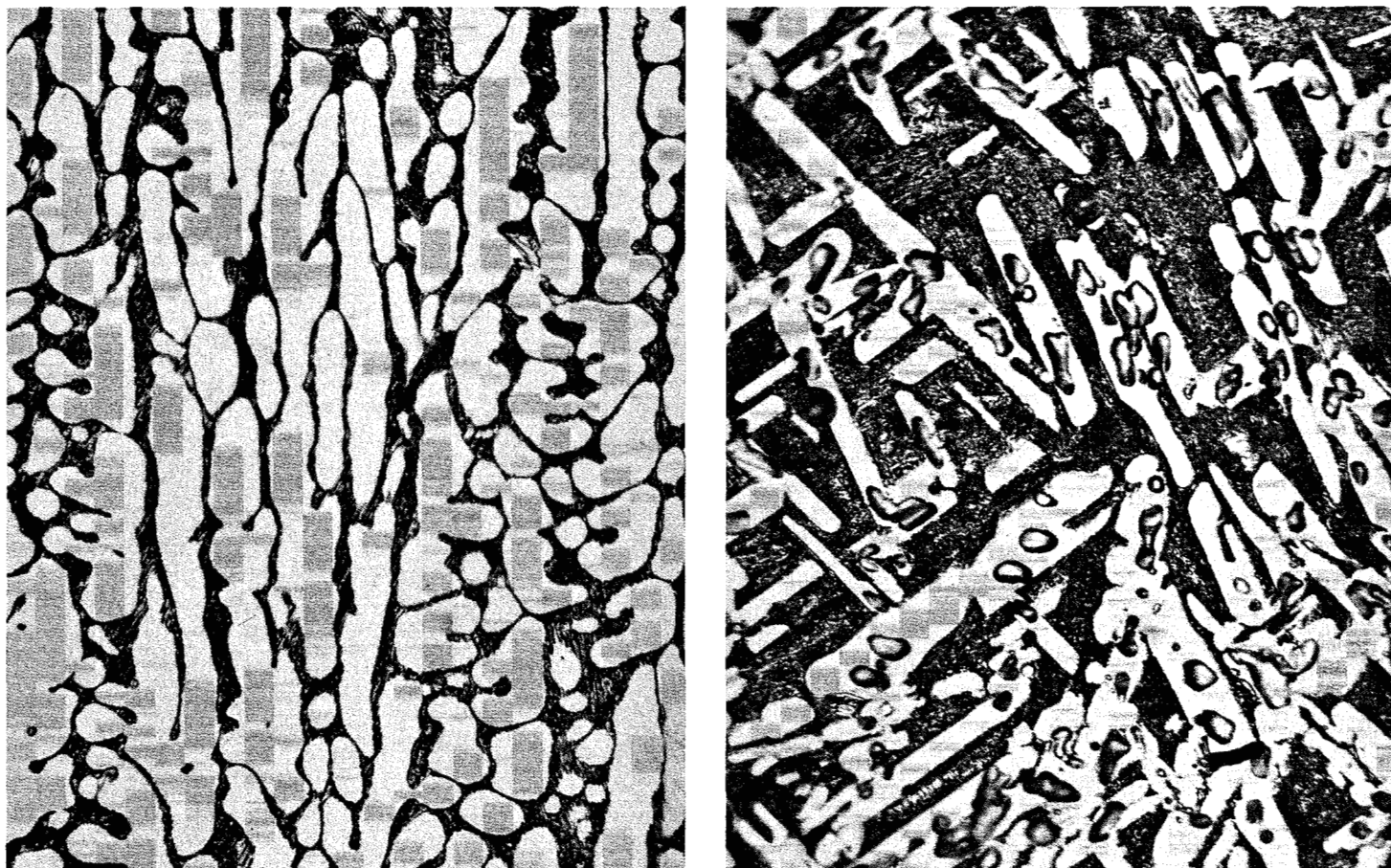

Fig. 9. Measured values of the Debye temperature θ_D and the electronic specific heat parameter γ are shown for various compositions in the Y-Ir system. The electronic specific heat remains fairly constant, whereas the Debye temperature falls rapidly to a minimum and rises again as more yttrium is added to the iridium.

Fig. 10. Metallographic photographs of the various Y-Ir system compositions. The eutectic is visible in all four photographs as the darker regions. At left, this page ($Y_{.05}Ir_{.95}$), the light areas are pure iridium. As more yttrium is added to the system [at right ($Y_{.20}Ir_{.80}$)], the amount of eutectic increases; the light areas are probably pure iridium but the precise identification has not been made.

The x-ray diffraction studies indicated that in compositions up to 10 atomic per cent yttrium only one phase appeared to be present, a cubic lattice of iridium containing less than 1 atomic per cent yttrium. At this point, we believed that the iridium cubic phase was the superconductor, but two questions remained unanswered. Why do increases in the yttrium concentration cause increases in the amount of superconducting phase, and where is the excess yttrium located? The excess yttrium neither enters the iridium lattice nor forms enough of a second phase to account for more than a small fraction of the yttrium present. The mystery of the missing yttrium was solved when we examined the microstructure of the samples using conventional optical metallography and transmission electron microscopy. Microscopic examination showed that a fine-grained eutectic (Fig. 10) was present in all samples and that the amount of the eutectic increased in direct propor-

tion to the increase in the amount of bulk superconductor as determined by the low-temperature specific heat measurements. The x-ray results, the metallographic data, and the low-temperature specific heat measurements allow no other conclusion. The bulk enhanced superconductivity is associated with the eutectic and results from the extreme decrease in the lattice stiffness. The failure of the x-ray diffraction studies to detect the eutectic is surprising; it suggests that the structure must consist of extremely small crystallites.

Search for High-Temperature Superconductors

The search for methods to produce higher T_c materials has been the subject of innumerable investigations ever since superconductivity was first observed. It has taken such widely different approaches as the attempts of Little (1964)

to produce superconducting polymers, the studies of Abeles and coworkers (1966) on the effect of granular material on T_c, and the suggestion of Ginzburg (1968) on raising T_c by the formation of metal-dielectric sandwiches. Unfortunately, to date essentially no success has resulted from all these attempts.

With the development of the BCS theory, T_c was related to θ_D, $N(0)$, and V, the electron-phonon interaction parameter, as shown in Eq. (7). On this basis, a material with high θ_D, $N(0)$, and V values should have a high T_c. Unfortunately, V is not known for most materials and cannot be determined from other parameters. When V was ignored, it appeared that materials with high θ_D and $N(0)$ values would be high-temperature superconductors. Limited success was achieved in relating high $N(0)$ values to high T_c. The dependence of T_c on θ_D appears to be much more complex. We find many examples that support a correlation between high T_c
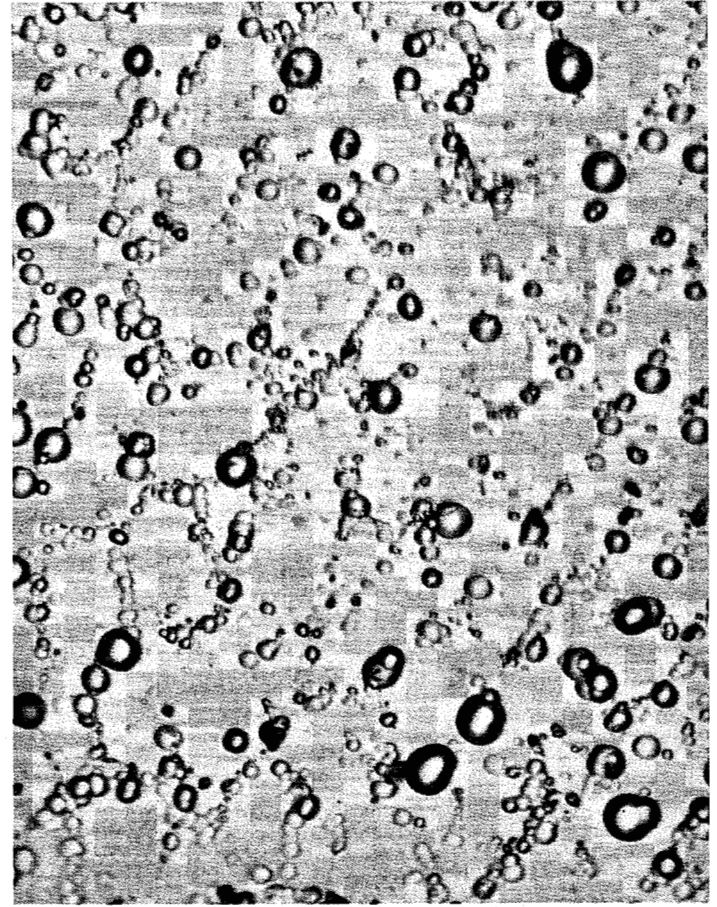
With further increase of yttrium [at left, this page ($Y_{.25}Ir_{.75}$)] the amount of eutectic begins to decrease; the light areas are probably YIr_2. At the right ($Y_{.30}Ir_{.70}$), the eutectic, the dark bubble-like structures, has almost disappeared. The lighter areas are YIr_2. The amount of eutectic for each composition is proportional to the percentage of material that is superconducting as measured by specific heat measurements. (1000X) Metallography by Ramiro A. Pereysa.

and high θ_D and many that contradict it. Technetium ($\theta_D = 454$ K) has a T_c of 8.9 K, whereas thallium ($\theta_D = 78$ K) has a T_c of 2.4 K. On the other hand, osmium ($\theta_D = 500$ K) has a T_c of only 0.66 K, whereas lead ($\theta_D = 108$ K) has a T_c of 7.2 K. The present belief is that the electron-phonon interaction parameter V and the Debye temperature θ_D are interrelated: V varies inversely with θ_D. The dependence of V on θ_D is not surprising since the electron-phonon interaction obviously varies with the lattice phonon frequency spectrum. Thus superconductivity should be favored in materials with high $N(0)$ and/or low θ_D values.

Other investigators have observed T_c enhancement, but never to the extent found in the Y-Ir system. Some enhancement occurs in dilute alloys of titanium, zirconium, or hafnium with the transition metals of groups V to VIII. Of particular interest is the investigation of the Ti-Mo system by Collings and Ho

(1969). They found that the T_c of the α' phase increased gradually from 1.5 to 6 K as the molybdenum concentration was increased up to 4.5 atomic per cent. Low-temperature specific heat measurements indicated an increase in γ and a decrease in θ_D, whereas metallographic examination showed that a hexagonal-close-packed martensitic structure was forming. Because the increase in γ and, therefore, in $N(0)$ was not sufficient to explain the increase in T_c, part of the enhancement was attributed to the lattice softening shown by the drop in θ_D. However, since both γ and θ_D were changing, the cause of the T_c enhancement was unclear.

In the Y-Ir system the situation is more straightforward. Because γ remained essentially unchanged while θ_D decreased, we can attribute the 30-fold increase in T_c directly to the modification of the lattice vibrations in the eutectic as compared to the vibrations in the iridium. This is the first documented case

of a system where the effects of θ_D and $N(0)$ can be separated clearly and the enhanced T_c can be linked directly to the change in the lattice vibrations. Changing the lattice vibrations has been anticipated theoretically as a means to enhance superconductivity. However, the experimental search involved making tiny spheres. The belief was that the vibration patterns of only a few hundred atoms would be severely altered compared to the vibration patterns of the same atoms located in an essentially infinite matrix of the same material. The alteration should result in a dramatic change in the Debye temperature, similar to the change observed in the eutectic. Although it is mere speculation at this time, the possibility that the eutectic in the Y-Ir system is made up of tiny regions of well-ordered atoms that are only slightly affected by the neighboring regions should be considered. If that is so, then the eutectic may well be a bulk form of an ensemble of small particles.
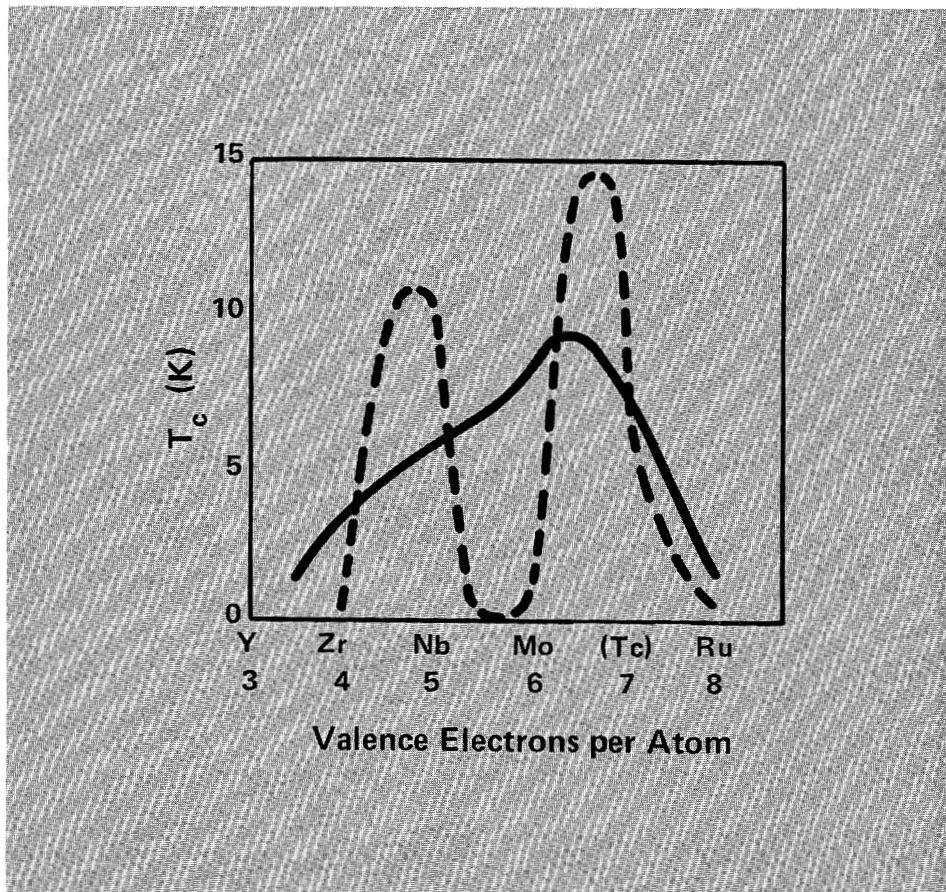
Fig. 11. The variation in T_c as a function of e/a for amorphous 4d transition metal alloys is shown by the solid line. The corresponding data for the same materials prepared in crystalline form are shown by the dashed curve. The distinct peaks for the crystalline materials have been broadened by preparing the materials in an amorphous state. The electronic levels appear to be blurred by the breakup of the crystalline structure.

Many implications now can be investigated. Within the field of superconductivity, the most obvious impact may be on amorphous materials. By definition, amorphous materials are disordered and noncrystalline; therefore their properties should be unaltered by radiation damage. Amorphous superconductors have been studied extensively as candidate materials for superconducting magnets in magnetic fusion reactors. Unfortunately, amorphous materials have low T_c. However, eutectics with high T_c and extremely small crystalline structures should exhibit similar resistance to radiation damage and should be useful in magnetic fusion applications.

Our work on eutectics suggests why amorphous materials have low T_c. Figure 2 shows the relationship between T_c and the e/a ratio for materials in crystalline form. When Matthias searched among the known superconductors for a relationship between T_c and the e/a ratio, he found two sharp peaks in the T_c curve at e/a ratios of 4.7 and 6.5 with sharp minimums between the peaks. These variations reflect the variation of $N(0)$ in the elements and alloys across the periodic table. When Colver and Hammond (1973) prepared the same materials in the amorphous state, they found the peaks simply broadened. That is, the high T_c values were lowered and the low values were increased (Fig. 11). The simplest explanation of this result is that the sharp maxima in $N(0)$ at certain compositions are blurred by the microscopic, liquid-like randomness of the atoms. To achieve high T_c in alloys, the $N(0)$ blurring must be avoided. The eutectic may be the method of accomplishing this. The microscopic structure of many eutectics can be changed dramatically by varying their solidification conditions. Their particle size varies strongly with cooling

THE AUTHORS

rates and approaches the amorphous state with very rapid quenches. These changes in structure cause changes in many of the magnetic, mechanical, optical, and thermal properties. As has been demonstrated in the Y-Ir system, it should be possible to prepare eutectics with regions of crystallinity large enough to keep the $N(0)$ large and sharp, but small enough to ensure that the Debye temperatures are lowered dramatically. Such preparations could lead to much higher T_c materials and provide a tremendous impetus to the widespread application of superconductivity.

Understanding Eutectics

The results of the present study may prove to be even more important outside the field of superconductivity. In metallurgy, eutectics have been known and studied for a long time without real progress in understanding when they occur and why they have such altered properties. The lowering of a melting point by mixing one substance with another has been known for a long time—but not understood. No theory or even hypothesis will predict the occurrence of eutectics. Now, the enhancement of T_c for the first time opens the way to a basic understanding of eutectics. We now realize that lattice softening goes hand in hand with the melting point minimum in the eutectics. We now have an important new piece in the puzzle of eutectic behavior.

The world has relied on eutectics for a long time, from getting rid of ice with salt to making soft solder, and from welding, to alkaline liquid coolants in reactors. Finally, some understanding is on the way; with it comes the possibility of progress toward higher T_c, technologically more useful superconductors, and perhaps eventually a better understanding of many metallic alloys.
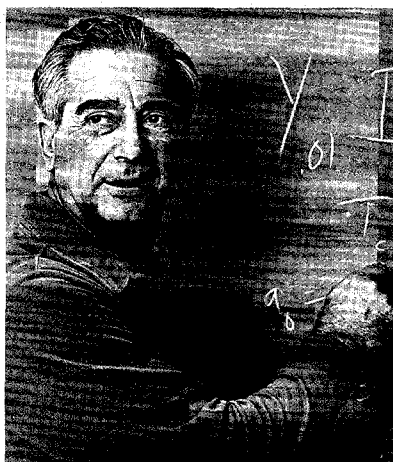
Angelo L. Giorgi earned his bachelor of science degree in chemistry in 1939, came to LASL in 1946, and received his Ph.D. in physical chemistry from the University of New Mexico in 1956. He has over 30 years of varied experience in research, development, and instrumentation in the fields of electrochemistry, radiochemistry, high-temperature phase studies, and cryogenics. His continuing investigations of superconducting and magnetic properties of various carbides and intermetallic compounds have resulted in discoveries of several new superconductors, a new itinerant electron ferromagnet, and the first itinerant antiferromagnet.

Gregory R. Stewart earned his bachelor of science degree cum laude from California Institute of Technology in 1971, and received his Ph.D. from Stanford University in 1975. He did postdoctoral work at Stanford and at the University of Kostanz, FRG. He joined LASL's CMB Division as a Staff Member in 1977, where he developed a new type of small-sample calorimeter and constructed a 7-T superconducting magnet. He is involved in characterizing new materials that range from high T_c superconductors of technological interest to lower T_c superconductors, where the interest is in understanding what makes superconductivity occur.

James L. Smith is best known for his definitive work on three of the five known superconducting actinides. He also has studied high-pressure phase transitions of americium. As an offshoot of the work described in the article, he has made interesting discoveries about dilute magnetism; for example, he has discovered magnets that are 100 times more dilute than any found before. He earned his bachelor of science degree at Wayne State University in 1965 and his Ph.D. in physics from Brown University in 1974. He has been a Staff Member in LASL's CMB Division since 1973.

Bernd T. Matthias is Associate Director of the Institute for Pure and Applied Physical Sciences and Professor of Physics at the University of California at San Diego, and part-time member of the technical staff of Bell Telephone Laboratories, Inc. He has been a consultant for LASL since 1957 and was named a Fellow of the Los Alamos Scientific Laboratory in 1971. He is a world authority on superconducting materials, having been involved in the discovery of more of these than any other individual. He is also well known for his discoveries of ferroelectrics and ferromagnets, and for his work on the questions of the coexistence of magnetism and superconductivity. He is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, and the Swiss Physical Society and a Fellow of both the American Physical Society and the American Association for the Advancement of Science. Matthias has received many scientific honors and awards, the two most recent awards being the Oliver E. Buckley Solid State Physics Prize in 1970, and American Physical Society International Prize for New Materials in 1979. The latter was for discovering unusually high temperature superconducting intermetallic compounds and alloys and demonstrating their usefulness in producing high magnetic fields for electric power technology and magnetic confinement of plasma. Originally from Frankfurt, Germany, he earned his Ph.D. from the Swiss Federal Institute of Technology in 1943.