<Transmission electron micrograph of the yttrium-iridium system at the composition $Y_{.05}$ $Ir_{.95}$(24 000X). TEM by Dorothy S. Garinger.

High-Temperature Superconductivity: A Metallurgical Approach

by Angelo L. Giorgi, Gregory R. Stewart, James L. Smith, and Bernd T. Matthias

A mysterious 30-fold enhancement of the critical temperature in the yttrium-iridium system has been traced to the formation of a eutectic structure and to a dramatic decrease in the stiffness of the crystal lattice.

Superconductivity is the sudden complete disappearance of electrical resistance in some materials when they are cooled below a critical temperature. This phenomenon (Fig. 1) has intrigued solid-state scientists, metallurgists, and engineers ever since its discovery by Kammerlingh Onnes in 1911. Visions of many possible applications of superconductivity to electrical power generation and distribution, fusion reactors, high-energy particle accelerators, and propulsion systems, and of the many new superconducting devices have provided a powerful stimulus to the search for superconducting materials with high superconducting critical temperature (T_c). Development of a microscopic theory on superconductivity (the BCS theory) in 1957 brought hope that the theory would prove useful in predicting new high T_c materials. Unfortunately, none of the predictions have been successful. Many of the new high T_c superconductors shown in Table I, which form the basis for the present superconducting

technology, were discovered by application of Matthias' Rule, an empirical rule developed in the 1950s. This rule relates the T_c of elements, alloys, and compounds to their average number of valence electrons per atom (e/a) as shown in Fig. 2.

In 1964, when workers at the Bell Laboratories were examining mixtures of the two metals yttrium and iridium as part of a study of the relationship between the T_c and the e/a ratio, they made a puzzling observation. When they added as little as 1 atomic per cent yttrium to iridium, the temperature at which the material became a superconductor quickly increased from 0.1 K to above 3 K. When they increased the amount of yttrium to 33 atomic per cent, the T_c remained at 3 K. What was causing this 30-fold increase in the superconducting critical temperature? The enhanced superconductivity was certainly not due to the small change in the e/a ratio produced by the addition of yttrium, nor could it be explained from the known materials in the system. The iridium T_c is
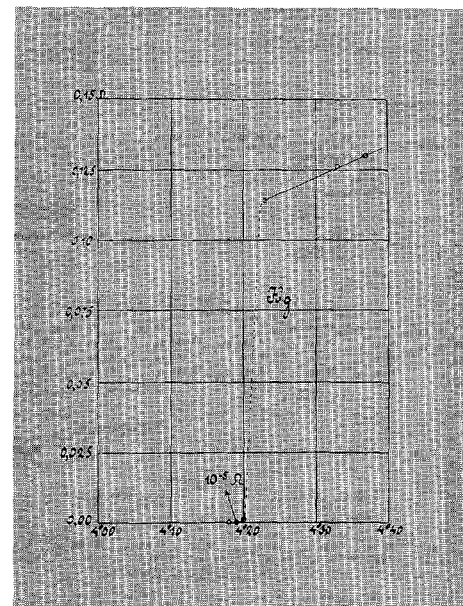

Fig. 1. A reproduction of Onnes' original data, which marked the discovery of superconductivity in 1911. The plot of resistance in ohms vs absolute temperature shows the complete disappearance of electrical resistance in mercury at 4.2 K.

only 0.1 K, and neither yttrium nor YIr_2 (the only known compound in the system) become superconductors even when they are cooled to 0.3 K. The immediate conclusion was that another compound, probably with a composition close to YIr_4, must exist and that this hypothetical phase was the source of the superconductivity. Many samples, prepared with compositions varying between iridium and YIr_2, were heat treated and examined by x-ray diffraction. All attempts to discover a new phase were unsuccessful. The source of the enhanced superconductivity

TABLE I

HIGH T_c SUPERCONDUCTORS

Compound	T_c (K)	Compound	T_c (K)
Nb_3Ge	23.2	$NbC_{.25}N_{.75}$	17.8
Nb_3Ga	20.3	Nb_3Al	18.8
$Nb_3Al_{.8}Ge_{.2}$	20.1	V_3Ga	16.5
Nb_3Sn	18.1	V_3Si	17.1

Fig. 2. Empirical behavior of T_c as a function of the average number of valence electrons per atom (e/a) for pure elements and alloys. This empirical relationship was discovered by B. T. Matthias in 1957.
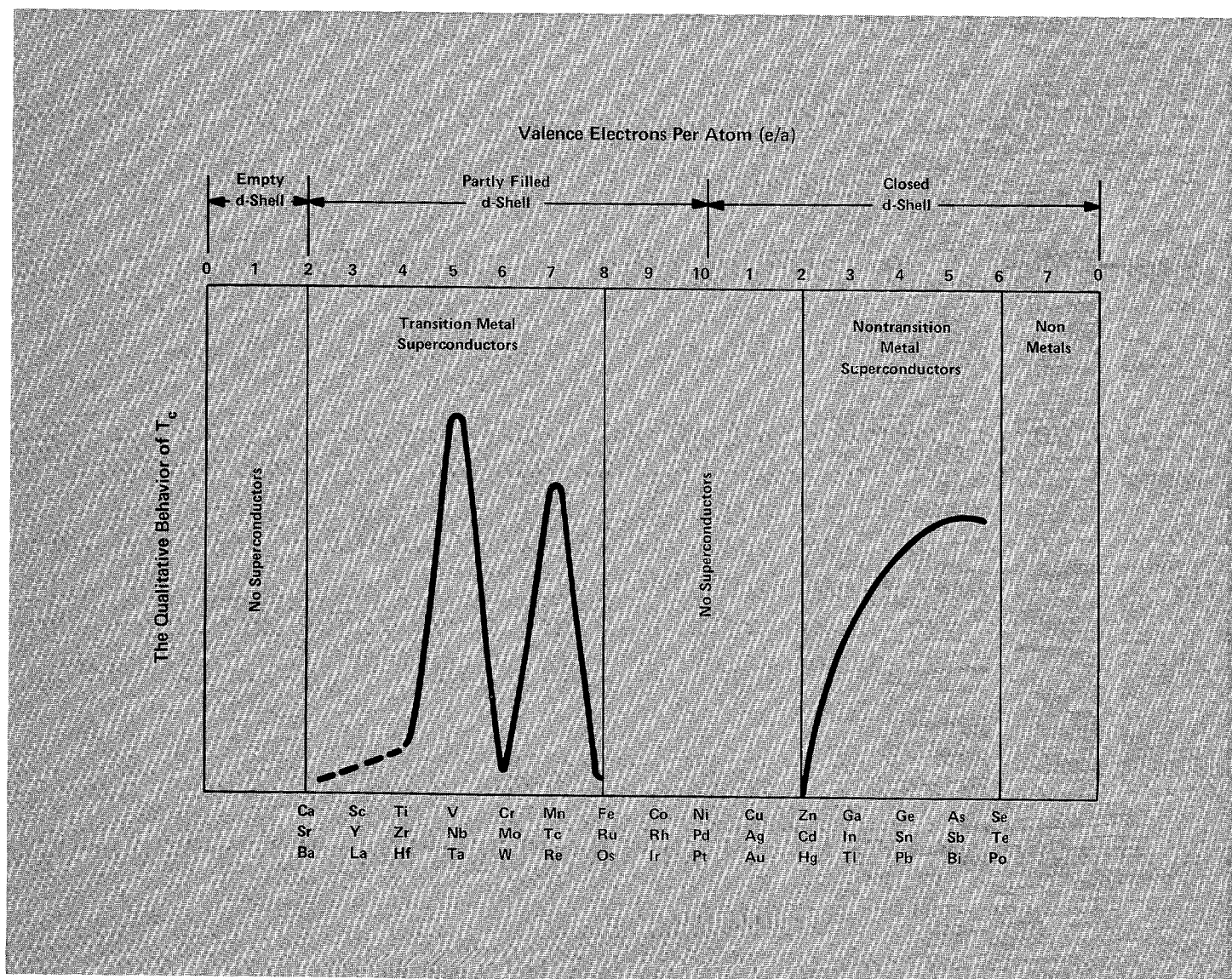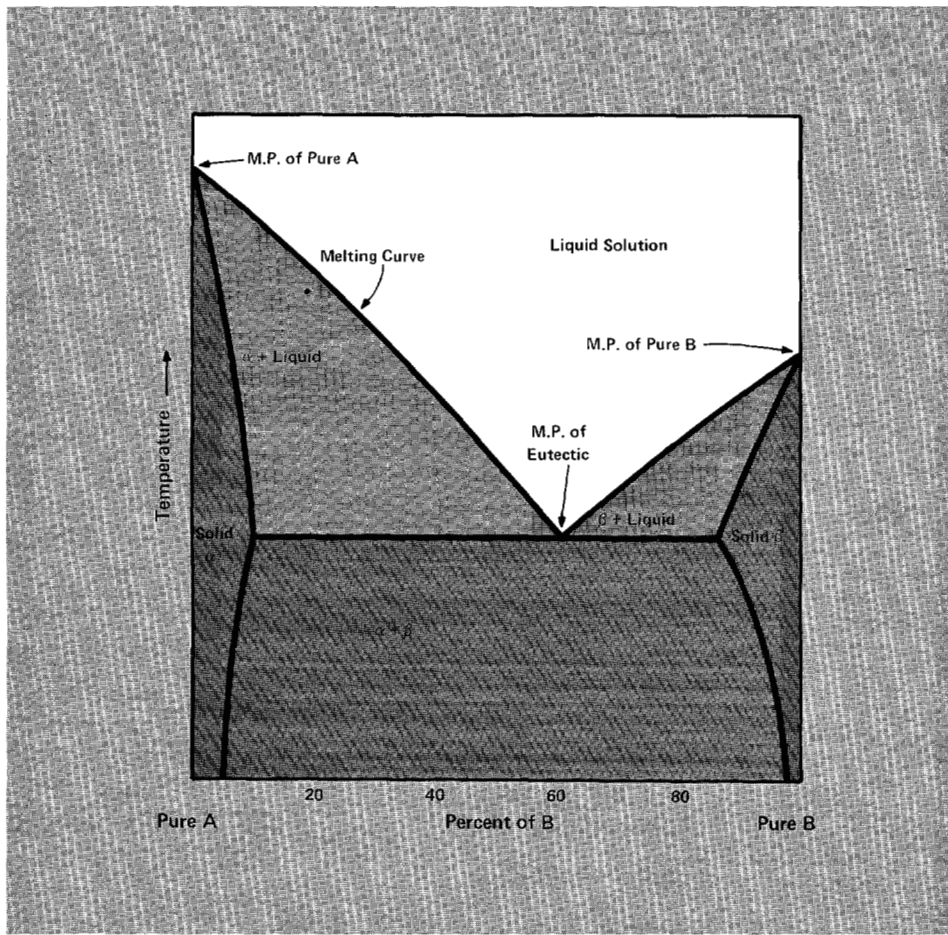
Fig. 3. A typical phase diagram for a mixture of metals showing melting point (M.P.) minimum at the eutectic composition. Solution of B into A lowers the M.P. of A; similarly, solution of A into B lowers the M.P. of B. Solid α is a solid solution of B atoms dissolved in the crystal lattice of A. Solid β is a solid solution of A atoms in the crystal lattice of B.

remained a mystery. The investigation was finally abandoned and all but forgotten.

This year, when interest in the Y-Ir system was revived, a much more thorough study was conducted at the Los Alamos Scientific Laboratory (LASL) in collaboration with the University of California (UC) at La Jolla, California. The careful characterization of the various compositions was extended to include low-temperature specific heat measurements, metallographic examination, and transmission electron microscopy as well as the usual x-ray diffraction and magnetic susceptibility measurements. From this study, we have learned that the source of the enhanced superconductivity in the Y-Ir system is a eutectic structure consisting of a mixture of iridium and the neighboring phase, YIr_2.

A eutectic is the unique mixture of two constituents, usually metals, that has the lowest melting point. Eutectics have been known since the days of the Roman Empire and have been in continued use since then. Bronze and solder are common examples. A typical phase diagram for a eutectic mixture is shown in Fig. 3. The melting point for the eutectic composition is considerably lower than for either constituent.

The low-temperature specific heat measurements on the Y-Ir samples disclosed that, with the formation of the eutectic structure, the stiffness of the lattice decreases dramatically. The enhanced superconductivity probably is a result of the lattice softening. This intriguing solution to the mystery promises a new investigative approach to high-temperature superconductivity.

Measurement Techniques

Reviewing some of the techniques used to measure the superconducting critical temperature will help explain the problems associated with a study of this type. At present there are over a thousand known superconducting materials. Their critical temperatures range from minimum values of a few millidegrees above absolute zero to the present maximum value of 23.2 K. Most of these materials are intermetallic alloys; that is, they are mixtures, compounds, or solid solutions of two or more metals.

The three methods used most commonly to determine superconductivity in such materials are based on three distinctive thermal and electromagnetic properties of the superconducting state:

1. The complete disappearance of electrical resistance.
2. The complete exclusion of magnetic fields, up to some critical value H_c, from the body of the superconductor.
3. A sharp increase in the electronic specific heat of the superconductor at T_c owing to the marked decrease in the entropy.

In the method based on resistance, the sample is fashioned into a rod or wire and a fixed current is passed through it. As the temperature is lowered, the voltage across the sample is monitored by the four-probe technique illustrated in Fig. 4. When the material becomes
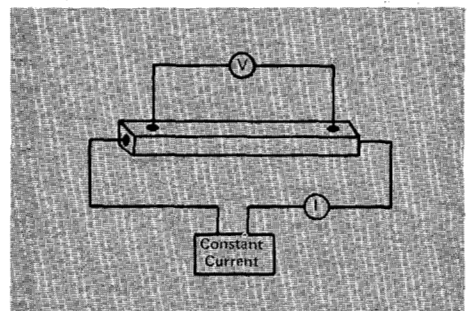

Fig. 4. Four-probe technique for measuring the change in electrical resistance as a sample becomes superconducting.

superconducting, the resistance and, therefore, the voltage suddenly drops to zero. The temperature at which the drop occurs is the T_c of the material. This method suffers from a demonstrated weakness. It requires a continuous superconducting path across the material, and it gives no indication of how much of the material is superconducting. Quite often the bulk of a material is not superconducting but instead contains microscopic filaments in a superconducting phase. A resistive measurement on such a sample gives results similar to those for a true bulk superconductor because the filaments, having zero resistance, short-circuit the sample and cause the voltage to drop to zero. Using x-ray diffraction to determine the phases present in a sample also can be misleading. If, as is often the case, the filaments in the superconducting phase represent only a small fraction of the total sample, their concentration may lie below the detection limit, and the x-ray diffraction pattern will indicate that the nonsuperconducting bulk material is the only phase present. An investigation limited to these techniques can lead to the erroneous conclusion that the phase representing the bulk material is the superconductor.

A much more widely used technique is the ac susceptibility method, based on the exclusion of magnetic fields (Fig. 5). A stable alternating current of less than 60 hertz is applied to the primary of a sensing coil. The output from two matched secondary coils, connected in opposition, is fed to the input of a frequency-locked amplifier. A small variable mutual inductance is connected between the primary and secondary circuits and adjusted to cancel out any residual imbalance in the secondary circuit. The sample, which can be a powder or solid, is placed in one of the secondary coils and cooled slowly. A sharp change in the sample's magnetic permeability at T_c causes an imbalance in
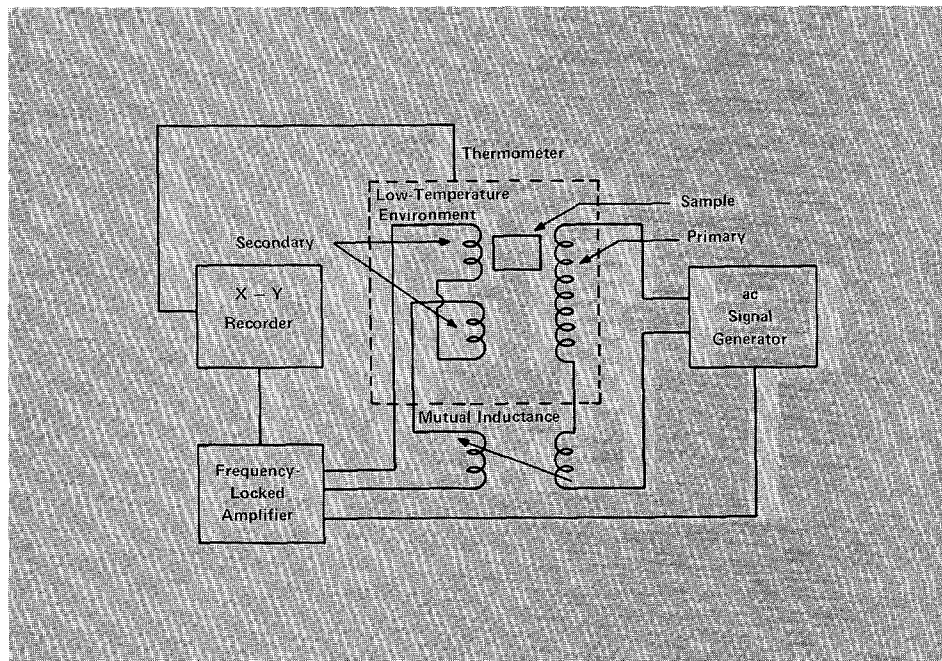

Fig. 5. Technique for measuring the change in magnetic permeability of a sample when it becomes superconducting. A rapid change in the electrical signal from the secondary coils caused by expulsion of the magnetic field from the sample indicates the onset of superconductivity.

the secondary circuit, which results in a signal at the output of the amplifier. Because the signal is proportional to the change in magnetic permeability, it gives a semiquantitative value of the amount of superconductor in the sample.

The ac susceptibility method is preferred over the resistive method because it detects superconductivity in the individual particles and does not depend on a continuous superconducting path. However, even this method can give misleading results. Occasionally, a superconducting phase is deposited as a thin film at the grain boundaries of a bulk material. When the film completely encloses the grains, it acts as a superconducting can; that is, it prevents any magnetic flux from penetrating into the canned bulk material. Under these conditions, the signal strength from the amplifier suggests that all the material is superconducting.

The method generally accepted as giving a true indication of both the presence and amount of superconducting material is measurement of the variation of the low-temperature specific heat with temperature (Fig. 6). The specific heat (C) is the amount of energy (dQ) required to raise the temperature of a unit mass (usually a mole) of material by a small increment (dT).

$$C = dQ/dT . \qquad (1)$$

The specific heat of a metal has two contributions, one from the thermal motion of the electrons surrounding the lattice and one from the lattice vibrations. For a normal metal, the two contributions to the specific heat C_n have a well-known temperature dependence.

$$C_n = \gamma T + \beta T^3 , \qquad (2)$$

where γ depends on the properties of the electrons and β depends on the crystal lattice. As shown in Fig. 7, these parameters are determined by plotting C_n/T vs T^2. The slope of the resulting straight-line-curve is equal to β and the intercept is γ. The information about the normal-state properties contained in these two parameters is discussed later.

When the metal becomes superconducting, the lattice contributions to the specific heat (βT^3) remain the same, but the electronic contributions (γT) change dramatically. The specific heat (C_s) for the superconducting phase is given by

$$C_s = ae^{-\Delta/kT} + \beta T^3 . \qquad (3)$$

The electronic term for a superconductor is clearly different in temperature dependence. The difference is due to the for-

mation, at T_c, of an energy gap (Δ) in the allowable energy levels that the electrons can occupy in the material. Bound electron pairs of opposite spin and momentum (Cooper pairs) form at T_c and occupy energy levels below the energy gap. Energy is needed to break up the pairs and raise them to energy levels above the energy gap. Since $ae^{-\Delta/kT}$ is usually more than twice as large as γT, the change in the electronic contributions at T_c causes a marked discontinuity in the specific heat curve (Fig. 7). The discontinuity is the best indication of the presence of a superconducting state.

A generally accepted result of the BCS theory is that, for 100% bulk superconductivity,

$$ae^{-\Delta/kT_c}/\gamma T_c = 2.43 . \qquad (4)$$

Thus the ratio of the electronic specific heats at T_c can be used to estimate the amount of the sample that has become superconducting and to rule out ambiguities caused by either microscopic amounts of one-dimensional paths in the resistive method or two-dimensional grain boundary cans in the ac susceptibility method. Further, if x-ray diffraction indicates the presence of a second phase, the amount of second phase estimated from a comparison of the relative intensities of the diffraction patterns can also be compared to the ratio of the electronic contributions to the specific heat.

A much more accurate estimate of the amount of superconducting material is possible for materials with T_c values at least four times greater than the lowest temperature to which the specific heat can be measured (for example, a $T_c \geq$ 4.8 K and a lowest temperature of 1.2 K). The superconducting phase contributes significantly to the specific heat at T_c, but its contribution dies away exponentially as the temperature drops below T_c, when the only terms left in the specific heat behavior vs temperature expression are βT^3 and any γT contribution from nonsuperconducting material. The ratio of this remnant γT to the value of γT above T_c, where the sample is 100% nonsuperconducting, is the exact fraction of the material that is nonsuperconducting.
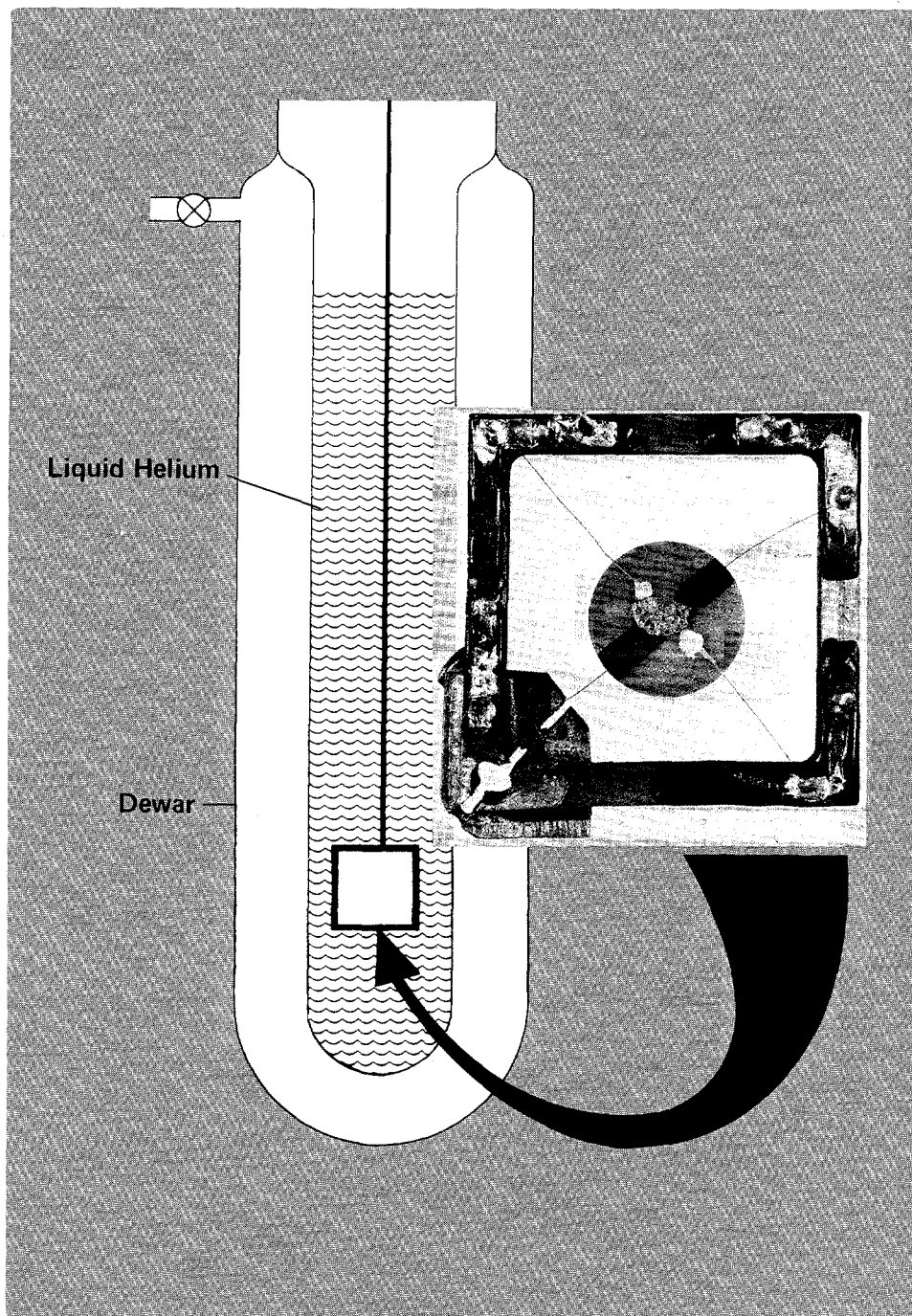

Fig. 6. Technique for measuring low-temperature specific heat. The sample, mounted on a sapphire disc 25 μm thick, is suspended in the center of a metal frame by 75-μm-diameter gold wires. The gold wires isolate the sample and platform thermally while providing two separate electrical connections to the metal frame. One connection supplies heat to the sample and platform through a film heater (the dark strip across the platform). The other connection measures the change in temperature by monitoring the change in resistivity of a germanium thermometer. The heat is supplied to the sample and platform in fixed increments by pulses of electrical energy to the film heater. Since sapphire is an excellent thermal conductor, sample and platform equilibrate rapidly after each pulse. By measuring the changes in temperatures for fixed increments in energy, the specific heat for the platform and sample is measured as a function of temperature. The total specific heat minus the known specific heat of the sapphire platform is the specific heat of the sample.