Pessimists and Optimists Discuss Superconductivity at Stanford

The late 1950's and early 1960's were truly the golden age for the study of superconductivity. On the theoretical side were the Bardeen–Cooper–Schrieffer equations, the Bogoliubov–Valentin transformations, the microscopic Gor'kov Green's-function approach, Aleksei Abrikosov's elegant type-II superconductivity theory, the theory of gapless superconductors with paramagnetic impurities, and the dc and ac Josephson effect. Experimentalists, for their part, developed tunneling techniques to study the density of states and the energy gap, observed flux quantization, detected both dc and ac Josephson quantum interference effects, discovered very high-field type-II superconductors and, concomitantly, developed superconducting high-field magnet technology. (For a review of the scientific and technological developments, see R. D. Parks, *Superconductivity*, Marcel Dekker, New York, 1969).

In little more than a decade the science of superconductivity, which had been one of the outstanding unsolved problems in solid-state physics, became one of the most mature and best understood areas of physics. The approaches involved some of the best successes of sophisticated many-body theory, as well as exacting and creative experimental techniques. From 26 to 29 Aug., the International Conference on the Science of Superconductivity took place, and nearly 450 registrants and over 100 observers came to Stanford University in sunny Palo Alto to appraise the science and the state of superconductivity. Many scientists admitted that they attended the meeting in part to confirm their suspicion that superconductivity, like so many other subfields of physics, was now entering a mature stage, a stage of detailed study rather than truly fundamental discoveries.

The Stanford conference will probably be remembered for its emphasis on the understanding of fluctuations in superconductors. The conference also indicated that the major hope for the future of superconductivity probably is wrapped up in the need to understand how to develop higher transition-temperature superconducting materials.

High-temperature superconductors

The most important feature of the conference and still the remaining outstanding technical problem is the attainment of higher transition temperatures, T_c. Physicists concerned with higher T_c can be divided into two classes—the optimists (mostly theorists) who believe that progress is being made and the pessimists (disappointed experimentalists) who have the facts on their side because, as yet, T_c has barely passed 20K. The elegant theory of William McMillan (Bell Telephone Laboratories) accounts for most electron–electron interactions and indicates that, if one could increase the strength of the normal phonon mechanisms, maximal T_c would be about 40K for V_3Si.

John Hopfield (Princeton University) presented his simple theory, which expresses the superconducting temperature of transition metals in terms of an atomic parameter and a mean phonon stiffness and does not involve the density of states as a relevant parameter. To obtain higher T_c, Hopfield recommends preparing superconductors in crystals that have an unusually low volume per atom ratio.

Excitonic mechanisms. A completely different approach to obtaining high T_c superconductors was presented by William Little (Stanford). He considered an excitonic mechanism in restrictive geometric structures and indicated that an effective attractive interaction between electrons can occur. Some experiments to construct hydrocarbon macromolecular systems and observe their excitation spectra were also described. In particular, with an optical-beam technique, Little examined the excitation spectrum of porphyrin compounds.

John Hulm (Westinghouse Research Laboratories) discussed high-temperature superconducting materials with the sodium-chloride structure, such as niobium nitride, niobium carbide and their alloys. Bernd Matthias (University of California, La Jolla) as usual berated the theorists by claiming that ". . . their theories have contributed relatively little to the actual raising of superconducting transition temperatures." Using the intuition for which he is so famous, Matthias predicted that, ultimately, extremely good crystals of $Nb_3Ge_{1-x}Al_x$ would have a transition temperature of 22.4K. He chastized the theorists again, to the glee of some experimentalists, for being able to adjust the theories to account for the lack of an isotope effect in ruthenium.

Immediately after Matthias's comments, a panel on high transition-temperature superconductors convened with Theodore Geballe (Stanford) as chairman. Vitali Ginzburg (Lebedev Institute, Moscow) jumped to the microphone and warned everyone not to be too pessimistic about high transition-temperature superconductors. Ginzburg felt sure that the imagination of the physicists had not been sufficiently applied to this problem and believes that some form of excitonic mechanism in layered structures or macromolecules might prove fruitful. Jokingly, he wished that all scientists who were too pessimistic about the attainment of high transition temperatures would be . . . (and while searching for the correct English verb, made a chopping motion with his hand to indicate "eliminated"). Ginzburg also has hopes for "metastable superconductors," in which long-lived excitons could be created in a semiconductor. These metastable excitons would then interact to form either a superfluid or a superconductor, depending on whether the pairing was between the electrons or the holes of the excitonic pairs.

The panel discussion confirmed the deep pessimism of some and the cautious optimism of others. The experimentalists had a "show me what to do" attitude. It was easy to see that if any physicist knew exactly how to raise T_c, he would be doing it himself rather than talking about it.

Astral superconductivity. In an invited talk, "Superfluidity and Superconductivity in Astrophysics," Ginzburg entertained the audience by discussing where in the universe super-

conductivity seems possible. For a superfluid boson system he required that T_λ, the temperature at which the system becomes superfluid, be lower than the melting temperature of the boson system. As examples of boson systems, he considered the possibility of superfluids of nuclei, alpha particles, photons and gravitons. For fermions, Ginzburg considered compressed metallic plasmas, neutron and proton fluids in neutron stars and neutrino seas. On the big planets of our solar system, such as Jupiter, the density of hydrogen at the surface can be in the metallic range with a possible transition temperature of a few hundred degrees. Ginzburg next considered superfluidity of neutrons and protons in neutron stars, where the energy gap can be as large as 10^{10} to 10^{11} Celsius degrees. The superfluidity of neutron stars would produce observable effects on the hydrodynamics of the neutron-star system.

Fluctuations in superconductors

Rolfe E. Glover (University of Maryland) discussed the effects of fluctuation on the electrical conductivity of thin films. Recent experiments have shown that the superconducting transition is not a step function of the temperature. Rather, it exhibits considerable rounding and tailing that can be detected and quantitatively related to fluctuation effects. In almost all thin-film samples examined by Glover, there was very good agreement between the experimental results and the phenomenological two-dimensional Aslamazov–Larkin theory for the conductivity σ.

$$\sigma_{\mathrm{fl}}{}^2(T) = e^2/(16\hbar d\,\tau)$$

Here σ_{fl} is the contribution to the conductivity due to fluctuation, d is the film thickness, e is the charge on the electron and $\tau = (T - T_c)/T_c$.

R. J. Warburton and Watt W. Webb (Cornell University) analyzed the effects of fluctuations on the resistive transition of pure and alloy tin whisker crystals with cross-section areas of 10^{-9} to 10^{-10} cm^2. They used the one-dimensional fluctuation theory of James Langer and Vinay Ambegaokar and Bertrand Halperin and D. E. McCumber. Bernard Serin and his coworkers at Rutgers University measured the fluctuation-induced changes in the extra conductivity as a function of magnetic field and temperature, and showed that $\sigma(H)/\sigma(0)$, the ratio of the conductivity at a given magnetic field to the conductivity at zero magnetic field, is a universal function of τ/H. This field behavior agrees with a calculation of Elihu Abrahams and coworkers (Rutgers) who, with a phenomenological time-dependent Ginzburg-Landau approach, determined the extra longitudinal conductivity that a thin superconducting sample exhibits in a magnetic field.

Theoretical inadequacies. Richard Thompson (Brookhaven) has recently shown that the Aslamazov–Larkin theory for fluctuations that is used by most experimentalists to analyze their thin-film data is incomplete. Additional contributions to the conductivity, discussed earlier by Kazumi Maki (Tohoku) must be included in the microscopic calculation and lead to a divergence of the conductivity rather than to the Aslamazov–Larkin result. A small magnetic field or electric current can help remove part of the divergence.

Ambegaokar (Cornell) reviewed the physical understanding of the effects of fluctuation on the electrical conductivity and magnetic susceptibility of superconductors near their transition temperature. As the temperature approaches T_c, Ambegaokar schematically separated the response function A into two parts

$$A = A_0 + A_{\mathrm{fl}}\,(1 + a_1\tau_c/\tau + \ldots)$$

where A_0 is a constant, A_{fl} is the contribution to the fluctuation far from the critical region, and corrections to the critical regions are governed by the magnitude of τ_c, where τ_c is some critical value for the relative temperature. Whether A_{fl} is observable or not depends on the magnitude of A_{fl}/A_0. If this ratio is large enough, the fluctuation can be seen over a wide range of temperature far from the critical region.

Ambegaokar pointed out that the Aslamazov–Larkin result giving a $(T - T_c)^{-1}$ temperature dependence for the conductivity of thin-film superconductors could not be thought of as analogous to the Curie–Weiss behavior of the susceptibility χ of a ferromagnet, because χ represents the fluctuations of the magnetization M, whereas σ is only indirectly coupled to the superconducting order parameter. For the region very close to T_c, S. Marčelja (University of Rochester) has added nonlinear terms to the conductivity equations. There is, however, no rigorous justification for this additional term.

Michael Tinkham and his group at Harvard University, and Lorin Vant-Hull (University of Houston) and James Mercereau (California Institute of Technology) observed a temperature-dependent enhanced diamagnetism above the transition temperature in bulk indium and tin that can be attributed to fluctuations in the susceptibility. The observed result for $M(H,T)$ agrees with a simple theory obtained by generalizing the Ginzburg–Landau equations to include magnetic-field effects. Evidence for fluctuations in bulk superconductors has been seen by Richard Hake (North American Rockwell). He measured magnetic-field dependence of the electrical resistivity in very dirty type-II superconducting alloys above the transition temperature.

Josephson tunneling

Michael Stephen (Rutgers) reviewed the effects of noise and fluctuations on the ac Josephson effect. The two most important sources of noise considered were the noise associated with dissipation within the cavity (photon shot noise), important at low T/T_c, and noise associated with the "normal" quasiparticle tunneling current, important near T_c. He also discussed the effect of noise on the linewidth and the spectrum of the voltage fluctuations. The presence of noise can be detected in the steps of constant voltage induced in a junction by monochromatic microwave radiation; it gives rise to a resistance that can be very small (width of less than 10^{-17} volts). These effects are important when relating the observations of voltage steps to measurements of fundamental constants such as $e/2h$.

Amorphous films. Myron Strongin (Brookhaven) described the evaporation of thin films at cryogenic temperature, which leads to amorphous films. In soft metals one can account for the increase in T_c with the lowering or softening of the phonon frequencies. In transition metals the major effect of disordered thin films is to smooth the density of energy states. Thus for high-T_c materials with large peaks in the density of states, T_c decreases, whereas in lower-T_c materials with low $N(0)$ valleys ($N(0)$ is the density of states at the Fermi surface), T_c increases. In many situations the changes in T_c were shown to be crucially related to the substrate. Effects of softening the phonon modes in granular aluminum have been seen in tunneling measurements by Jean Klein and A. Leger (Centre Nationale de la Recherche Scientifique).

Benjamin Abeles (RCA Laboratories) described superconducting effects in amorphous aluminum that is evaporated in an oxygen atmosphere; this treatment leads to superconducting granules as small as 4 nanometers in diameter. The granules are believed to be coupled to one another through the oxide, which acts as a Josephson barrier or as a weak link.

Small particles. Ivar Giaever (General Electric) described a tunneling technique to study the superconducting properties of very small particles that are imbedded in the oxide layer of tunnel junctions. With a simple model that includes the capacitance of the small-particle superconductors, Giaever confirmed superconductivity without a significant change in T_c in particles down to 2.5-nm radius. Superconductivity in such small particles is very difficult to understand, because particles of this size have about 10^4 electrons; according to BCS theory only one out of every 10^4 electrons condenses into the superconducting ground state. In addition the quantized level spacing in such small particles is of the order of the energy gap itself.

Type-II superconductors

Serin reviewed the thermomagnetic properties of type-II superconductors, including the Hall effect, Peltier effect and Ettingshausen–Nernst effect near the upper critical field. The magnitude of these effects can be related to the entropy carried by moving fluxoids. Absolute agreement for transport coefficients in pure type-II superconductors between theory and experiment is poor; the experimental results, however, do correlate with the purity of the samples as predicted by the theory. For low fields the idea that vortices carry the entropy associated with their normal-like cores seems valid.

U. Essman (Max Planck Institute, Stuttgart) reviewed the technique he developed with H. Traüble for observing the flux lattice in type-II superconductors with powder patterns. He illustrated the beautiful triangular lattice one obtains in ideal type-II superconductors, but he emphasized new data that show an intermediate type-I superconducting behavior in a type-II superconductor. For type-II superconductors that have low κ values, G. Eilenburger and H. Büttner have demonstrated that an attractive interaction can exist between relatively well separated vortices and thus, when flux enters a superconductor, the induction will jump to a value that corresponds to the vortices being a fixed distance apart. With further increases in magnetic field, the induction should behave as does the usual mixed-state type-II magnetization.

William Vinen (University of Birmingham) discussed thermal conduction and ultrasonic absorption in type-II superconductors for fairly clean samples and low magnetic field. In this limit, the flux vortices can be treated as relatively isolated. The scattering of electrons and phonons includes an additional mechanism due to the spatial modulation of the order parameter by the vortices, and leads to the scattering of an electron into a hole excitation. The bound excitations in the core of the vortices do not seem to affect ultrasonic attenuation. Normal core effects, however, are observed in the thermal conductivity; here the frequency of thermal phonons is such that they can overcome any small gap present on the core.

Varying gap parameter. John Bardeen (University of Illinois) discussed the theory of transport in superconductors in which the gap parameter $\Delta\ (r,t)$ can vary in space and time. Bardeen discussed the current flow between normal and superconducting boundaries and the motion of vortex lines in pure type-II superconductors. The total effective field in the core of a vortex is due to two terms, one related to the pair-potential field and the other to the real magnetic field in the core. The sum of these two fields is approximately H_{c2}, the upper critical field. A magnetic-field value in the core equal to H_{c2} brings the Bardeen–Stephen theory into line both with the Nozieres–Vinen hydrodynamic model and with the experimental behavior of the Hall effect and other thermomagnetic measurements in type-II superconductors.

Maki reviewed recent progress in understanding the microscopic dynamics and the recent experimental consequences of vortex motion in type-II superconductors. The theory seems to work reasonably well for the flow resistance and thermal conductivity in the "dirty" limit; in the "clean" limit, however, there is significant disagreement between theory and experiment. The comparison of thermomagnetic effects that give the transport entropy of vortices in type-II superconductors is semiquantitatively correct and agrees with the observation that the entropy per vortex approaches zero at $T = 0$ and at $T = T_c$. Flux-flow resistance measurement by Yoshio Muto and his group (Tohoku) are in good agreement with Maki's theory for dirty type-II superconductors.

Metals and alloys

H. Hunter Hill (Los Alamos Scientific Laboratory) discussed superconductivity and magnetism in row seven of the periodic table (the actinide elements) and compared the results with both the transition and the rare-earth elements. The recently observed positive isotope effect in alpha uranium was discussed in detail. Hill suggested that interaction between conduction electrons and nuclear spin in U_{235} might decrease, in a manner similar to magnetic impurities, the transition temperature of U_{235} relative to U_{238} by as much as 0.05 Celsius degrees. The decrease in T_c would be enough to explain the anomalously large positive isotope effect observed. Further study on a third isotope should help resolve this point.

Magnetic impurities. T. Sugawara of the University of Tokyo reviewed our experimental and theoretical understanding of the effects of magnetic impurities on transition temperature and critical magnetic-field behavior of superconductors. Effects due to the Kondo anomaly in tunneling measurement on the density of energy states were also discussed for lanthanum–gadolinium, lanthanum–cerium and palladium–manganese alloys. The decrease in T_c disagreed significantly with the simple Abrikosov-Gor'kov theory; this disagreement indicates that the effects of Kondo scattering must be included.

S. Foner and his group at the Massachusetts Institute of Technology presented critical-field versus temperature data for the various nearly single-phase crystals of Nb_3Al. The crystal with the highest critical temperature, $T_c = 18.7K$, showed an increase in critical field with temperature, $(dH_{c2}/dT)_{T=T_c}$, to be 26 kG/K, and did not seem to display any effects from Pauli paramagnetic limiting. Foner also reported some preliminary pulsed-field measurements at 4.2K and predicted that the low-temperature critical field of Nb_3Al may well over 300 kG!

Peter Fulde (Frankfurt) and Alan Luther (Max Planck Institute, Munich) have theoretically treated the problem of a magnetic impurity that is subjected to a crystal field. Fulde believes that, combined with tunneling measurements, such techniques can be useful to investigate crystal fields in metals.

Expectations

It is very difficult to predict the future of the science of superconductivity. There will, no doubt, be important developments in applications of superconductivity, but truly large-scale use would require a significant breakthrough in the attainment of higher T_c superconductors or a re-evaluation of where high magnetic fields and superconducting devices can be commercially useful. Examples of present-day applications of superconducting technology, although limited to basic and applied physics research, were convincingly displayed in the tour of the Stanford linear accelerator facilities arranged by the conference committee.

It appears unlikely that, still hidden within the theory of superconductors, are surprises equivalent in importance to the Josephson effect. An interesting conjecture at the conference was Ginzburg's reference to "metastable superconductors." If Ginzburg is correct, or high T_c is obtained, or mechanisms other than the phonons are discovered to yield superconductivity, or an effect equivalent in importance to the Josephson effect is uncovered, it will be time to call another conference devoted to the *science* of superconductivity.

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