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EUGENE GARFIELD
INSTITUTE FOR SCIENTIFIC INFORMATION®
3501 MARKET ST., PHILADELPHIA, PA 19104

# Investigations of Chemical Reactions Lead to 1986 Nobel in Chemistry for John C. Polanyi, Dudley R. Herschbach, and Yuan T. Lee; In Physics, Ernst Ruska, Gerd Binnig, and Heinrich Rohrer Share Prize for Advances in Microscopy

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The work of the 1986 Nobel laureates in physics and chemistry illustrates the impact that new technologies and methods can have on research.[1] The 1986 awards also recognize research that has long-term impact dating as far back as the 1930s. In regard to the work of the chemistry winners, citation data demonstrate the continuing influence of research done during the 1960s and 1970s. In physics, the data demonstrate a contrast in the citation records of the researchers who shared the prize, as Alexander Grimwade, director, *ISI Atlas of Science®*, noted in a recent article in *The Scientist™*. The work of one of the physics winners, Ernst Ruska, from the first half of this century, has become so assimilated into scientific wisdom that explicit citations to it are rare. The two researchers who shared the other half of the physics prize published their work in the early 1980s. The citation impact was immediate.[2] Without a citation index for the prewar years we can't determine if this was the case for Ruska's work. However, there is little doubt it had a major and prompt impact on the development of biological science.

## Chemistry

The 1986 chemistry prize was shared by three researchers: John C. Polanyi, University of Toronto, Canada; Dudley R. Herschbach, Harvard University, Cambridge, Massachusetts; and Yuan T. Lee, University of California, Berkeley. According to the Royal Swedish Academy of Sciences, "Their work has been of great importance for the development of a new field of research in chemistry—reaction dynamics—and has provided a much more detailed understanding of how chemical reactions take place."[3] The wide scope of applications of this new understanding is evident in ISI®'s *Current Chemical Reactions®* (*CCR®*) *Personal Databases*, a structure-based reaction file of new synthetic methods that we discussed recently.[4] This product joins *Index Chemicus®* and *CCR* in providing students and professionals with important current awareness of new organic chemical compounds and pathways.

Polanyi's work in chemical reactions derived from a question he formulated as a graduate student: what types of forces operating during a molecular collision are the most conducive to reaction? In the process of answering this question, Polanyi developed a method known as infrared chemiluminescence, a means of measuring and analyzing the emission of energy from product molecules in chemical reactions. Polanyi's early work on chemiluminescence dates from the late 1950s, when he began studying the reaction $H + Cl_2 \rightarrow HCl + Cl$. Polanyi reasoned that a newly created hydrogen chloride molecule would come out of the reaction vibrating and rotating, eventually emitting energy in the form of infrared photons. Analysis of data from an infrared spectrometer confirmed that 50 percent of the liberated energy was emitted from very high-level vibrations in the hydrogen chloride molecule.[5] It is this information on the quantum mechanical states occupied by the product molecules that reveals the detailed behavior of a chemical reaction.

Polanyi was born in Berlin, Germany, in 1929 and received his PhD in chemistry at the University of Manchester, UK, in 1952. He has been professor of chemistry at the University of Toronto since 1962. Many *Current Contents®* readers will recognize his name since his father was Michael Polanyi, the chemist and philosopher whose works include the widely cited 1958 book *Personal Knowledge*, an "enquiry into the nature and justification of scientific knowledge."[6]

In 1966 Polanyi published one of his most-cited papers in the *Journal of Chemical Physics*. Coauthored with P.J. Kuntz and colleagues at the University of Toronto, it has been cited in over 270 publications. Two more of his most-cited papers appeared in 1972, one concerning "Some concepts in reaction dynamics," and another, coauthored with University of Toronto colleague K.B. Woodall, on the "Mechanism of rotational relaxation." (See Table 1 for a list of Polanyi's most-cited papers.) Polanyi has continued to develop the chemiluminescence technique and has provided valuable theoretical insights into the forms of energy at work in chemical reactions.[5]

Dudley R. Herschbach used another approach in exploring chemical reaction dynamics. Employing a method analogous to nuclear reaction studies by high-energy physicists, Herschbach explored molecular reactions by firing the reactant molecules at one another in two separate, well-collimated streams. This technique had been tried sporadically in chemistry since the 1930s, but Herschbach was the first to fully exploit its potential.[5] His first experiments, in the late 1950s, centered on potassium atoms reacting with methyl iodide. The equipment was crude; the detector consisted of a hot tungsten wire that gave off an electrical current when struck by potassium iodide molecules. Despite the relatively primitive apparatus, Herschbach and his colleagues were able to demonstrate that the reaction products merge with a strongly preferred range of directions and velocities. This result and later work have provided much information about the forces governing the making and breaking of chemical bonds.

Table 2 is a list of Herschbach's most-cited works. For example, a 1959 paper from the *Journal of Chemical Physics*, "Calculation of energy levels for internal torsion and over-all rotation. III," has been cited more than 300 times. Interestingly, this paper and the next three papers listed pertain to studies of molecular spectra and structure, which is outside Herschbach's major field of reaction dynamics. In a recent telephone interview, Herschbach noted that the high number of citations for these papers most likely reflects a difference in citing populations. There are more researchers involved in spectroscopy than are involved in collision dynamics, which, according to Herschbach, may have something to do with why these papers have been highly cited.[7] Herschbach's most-cited work, "Reactive scattering in molecular beams," a 1966 paper from *Advances in Chemical Physics*, has also received more than 300 citations.

Herschbach was born in San Jose, California, in 1932 and received a BS from Stanford University in 1954. In 1958 he received his PhD in chemical physics at Harvard, where he has taught chemistry since 1963. It is significant that one of his most-cited works, the 1959 paper mentioned above, came from his doctoral research.

Considerable advances in the crossed molecular beam method were made by Yuan T. Lee. The chemist joined Herschbach's team at Harvard in 1967 as a postdoctoral fellow and set about replacing the tungsten-wire detector with a mass spectrometer of his own design.[5] This device permitted analysis of a much broader class of reactions. Coupled with supersonic beam sources and laser beams, it greatly extended the applications of the molecular beam technique. Subsequently, at the University

**The most-cited papers from the *SCI®*, 1955-1986, for the 1986 Nobel laureates in chemistry. Number of citations and bibliographic data appear below. The *SCI* research front(s) to which the paper is core are included in parentheses.**

**Table 1:** John C. Polanyi's most-cited papers.

| Number of Citations | Bibliographic Data |
|---|---|
| 291 | **Polanyi J C.** Some concepts in reaction dynamics. *Account. Chem. Res.* 5:161-8, 1972. (74-1067, 75-0075, 76-0189, 79-2167, 86-7005) |
| 274 | **Kuntz P J, Nemeth E M, Polanyi J C, Rosner S D & Young C E.** Energy distribution among products of exothermic reactions. II. Repulsive, mixed, and attractive energy release. *J. Chem. Phys.* 44:1168-84, 1966. (70-0098, 71-0120, 72-0128, 73-1314, 74-0386, 75-0075, 76-0400) |
| 223 | **Polanyi J C & Woodall K B.** Mechanism of rotational relaxation. *J. Chem. Phys.* 56:1563-72, 1972. |
| 199 | **Polanyi J C & Woodall K B.** Energy distribution among reaction products. VI. $F+H_2$, $D_2$. *J. Chem. Phys.* 57:1574-86, 1972. (73-0064, 74-0386, 75-0075, 76-0400, 77-0548, 79-0509) |
| 182 | **Polanyi J C & Wong W H.** Location of energy barriers. I. Effect on the dynamics of reactions A+BC. *J. Chem. Phys.* 51:1439-69, 1969. (72-0128, 74-0386, 75-0075, 79-2167, 86-7005) |

**Table 2:** Dudley R. Herschbach's most-cited papers.

| | |
|---|---|
| 336 | **Herschbach D R.** Reactive scattering in molecular beams. *Advan. Chem. Phys.* 10:319-93, 1966. (71-0120, 73-1151) |
| 320 | **Herschbach D R.** Calculation of energy levels for internal torsion and over-all rotation. III. *J. Chem. Phys.* 31:91-108, 1959. (70-0858, 76-1326) |
| 247 | **Herschbach D R & Laurie V W.** Anharmonic potential constants and their dependence upon bond length. *J. Chem. Phys.* 35:458-63, 1961. (70-0149, 86-1482) |
| 173 | **Laurie V W & Herschbach D R.** Influence of vibrations on molecular structure determinations. II. Average structures derived from spectroscopic data. *J. Chem. Phys.* 37:1687-93, 1962. (76-1029) |
| 162 | **Herschbach D R & Laurie V W.** Influence of vibrations on molecular structure determinations. III. Inertial defects. *J. Chem. Phys.* 40:3142-53, 1964. |
| 123 | **Grice R & Herschbach D R.** Long-range configuration interaction of ionic and covalent states. *Mol. Phys.* 27:159-75, 1974. (84-1505) |
| 119 | **Herschbach D R.** Reactive scattering. *Faraday Discuss. Chem. Soc.* 55:233-51, 1973. (84-7269) |

**Table 3:** Yuan T. Lee's most-cited papers.

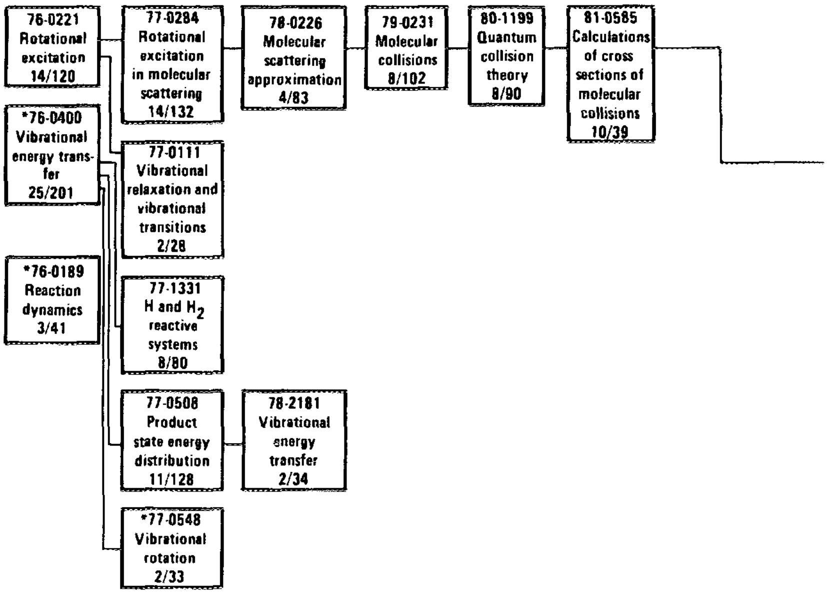
| | |
|---|---|
| 193 | **Barker J A, Watts R D, Lee J K, Schafer T P & Lee Y T.** Interatomic potentials for krypton and xenon. *J. Chem. Phys.* 61:3081-9, 1974. (76-0321, 77-0414, 82-0698, 84-1834, 85-0108) |
| 182 | **Schulz P A, Sudbo A S, Krajinovich D J, Kwok H S, Shen Y R & Lee Y T.** Multiphoton dissociation of polyatomic molecules. *Annu. Rev. Phys. Chem.* 30:379-409, 1979. (81-0490, 82-0454, 83-2876, 84-2835) |
| 148 | **Grant E R, Schulz P A, Sudbo A S, Shen Y R & Lee Y T.** Is multiphoton dissociation of molecules a statistical thermal process? *Phys. Rev. Lett.* 40:115-8, 1978. (79-0561, 80-0571, 81-0490) |
| 143 | **Coggiola M J, Schulz P A, Lee Y T & Shen Y R.** Molecular beam study of multiphoton dissociation of $SF_6$. *Phys. Rev. Lett.* 38:17-20, 1977. (78-0549, 79-0561) |
| 142 | **Chen C H, Siska P E & Lee Y T.** Intermolecular potentials from crossed beam differential elastic scattering measurements. VIII. HE+NE, HE+AR, HE+KR, and HE+XE. *J. Chem. Phys.* 59:601-10, 1973. |

of Chicago, Illinois, and in his present post at the University of California, Lee has continued to investigate reactions, designing and building increasingly sophisticated molecular beam machines.

Lee was born in Hsinchu, Taiwan, in 1936 and received a BS from the National Taiwan University, Taipei. He came to the University of California, Berkeley, as a graduate student in 1962, receiving his PhD in chemistry in 1965. After teaching in Cambridge and Chicago, Lee returned to Berkeley as a professor of chemistry in 1974, the same year he became a US citizen.

Table 3 lists Lee's most-cited papers. For example, "Interatomic potentials for krypton and xenon," a 1974 paper from the *Journal of Chemical Physics*, coauthored

Figure 1: Historiograph of research fronts relating to reaction dynamics, 1976-1986. Numbers of core/citing papers are indicated at the bottom of each box. Asterisks (*) indicate that Polanyi is a core author in that research front; daggers (†) indicate Herschbach is a core author.



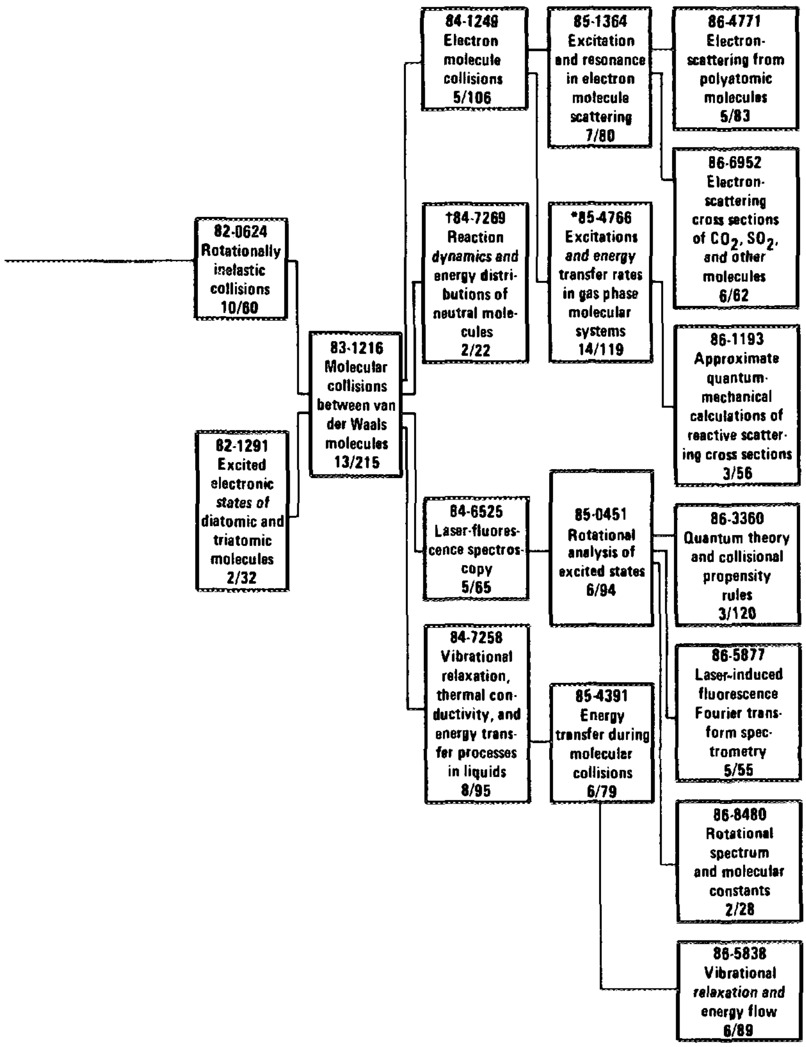

with J.A. Barker, IBM Research Laboratory, San Jose, California, and colleagues, has received nearly 200 citations.

The historiograph in Figure 1 shows the progression of research fronts relating to reaction dynamics from 1976 to 1986. One of these 1985 fronts, "Rotational analysis of excited states," #85-0451, is included in the higher-level map in Figure 2. This map shows the citation links between #85-0451 and the other fronts that make up the higher-level front "Laser and microwave spectroscopy of rotational and vibrational states in molecules," #85-0083.

The highly cited work of Polanyi and Herschbach continues to show up in our research fronts. Polanyi's most-cited paper is core to a 1986 research front, "Selectivity, reactivity, and equilibrium in molecular reaction dynamics," #86-7005. And Herschbach is in the core of another front, "Molecular mechanics—vibrational frequency and spectra," #86-1482. For those readers not familiar with the notion of research fronts in the context of co-citation analysis, see our discussion earlier this year of the new *ISI Atlas of Science*. As I noted, these fronts are crucial to our analysis of the emerging fields that receive first priority in the *Atlas*.[8]

## Physics

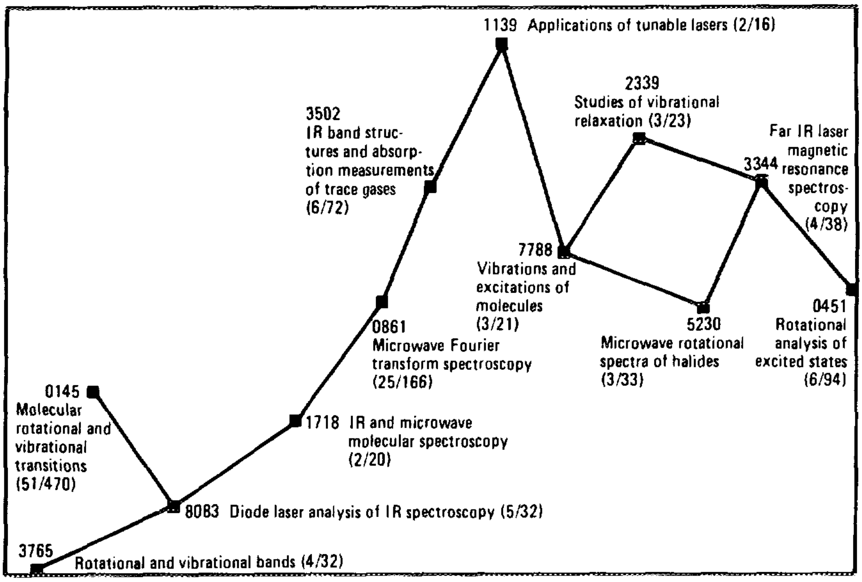
The physics prize was shared by Ernst Ruska, Fritz Haber Institute of the Max Planck Society, Berlin, Federal Republic of Germany, and by Gerd Binnig and Heinrich Rohrer, IBM Research Laboratory, Zurich, Switzerland. Ruska received the award for his work in electron optics and for the design of the electron microscope, which the Royal Swedish Academy referred to as "one of the most important inventions of the century."[9] Binnig and Rohrer received their portion of the prize for their design of the scanning tunneling microscope, an invention that has opened up "entirely new fields...for the study of the structure of matter."[9]




Ruska, born in Heidelberg in 1906, was honored for work done more than 50 years ago. After attending the Technical University in Munich, he became a graduate student at the Berlin Technical University. In his 1980 work *The Early Development of Electron Lenses and Electron Microscopy*, he discusses the steps leading to the electron microscope.[10] A key development was the discovery that electron beams could be used to produce an image of an object. As Ruska points out, electron beams promised to surpass the resolution possible in a light microscope, which is limited by the wavelength characteristics of light. A key finding was that a solenoidal magnetic field can be used as a lens to concentrate electron beams.[10] (p. 8)

Under teacher Max Knoll at the Berlin Technical University, Ruska began studying the electron-optical properties of magnetic coils, finding that a properly designed iron encapsulation improved these properties considerably.[11] Also, it then

**Figure 2:** Higher-level, multidimensional-scaling map for research front #85-0083, "Laser and microwave spectroscopy of rotational and vibrational states in molecules." Numbers in parentheses indicate the number of core/citing papers in each research front.




became possible to build a lens with a short focal length, which is a prerequisite for high magnification. In early 1931 Ruska and Knoll presented their design of what can be considered the first electron microscope, an apparatus using two magnetic coils in series.[12] The authors avoided the term "electron microscope," however, out of "fear of being accused of showmanship," as Ruska later wrote.[10] (p. 28) They did use the term in an article published in 1932.[13] In an article assessing 50 years of electron microscopy in biology, V.E. Cosslett, High Resolution Microscopy Group, University of Cambridge, UK, notes that Ruska's early work on the electron microscope "must rank as one of the most productive doctoral theses ever."[14]

Although the early designs were initially inferior to light microscopes in resolution, Ruska and colleagues made substantial improvements in electron microscopy. By the end of 1933, Ruska had obtained resolution that equaled and even surpassed that of a light microscope.[10] (p. 44) In 1937 Ruska accepted a post at Siemens laboratories, Berlin, where, with his brother Helmut, he persuaded the company to undertake development of the world's first commercially available, mass-produced electron microscope.

Although Ruska's work from the 1930s and 1940s predates the period covered by our database, citations to his early work continue to appear in the *Science Citation Index*®. And his 1980 history of electron microscopy[10] is one of nine core documents in the 1985 research front "History and development of electron microscopy," #85-2288.

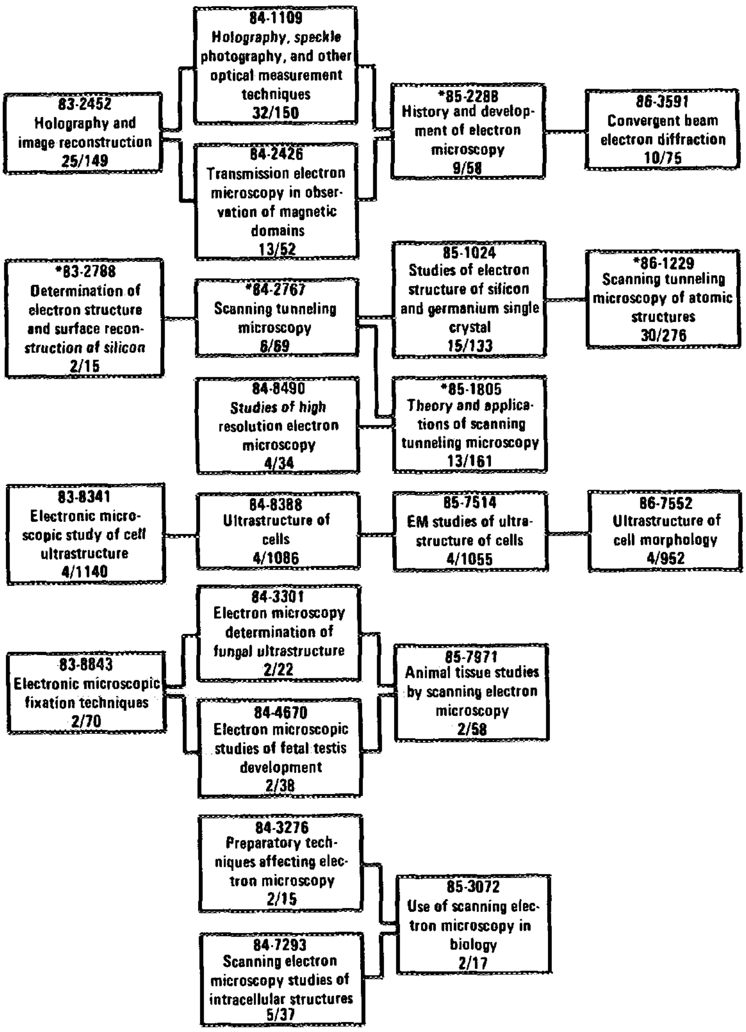
In 1955 Ruska became director of the Institute of Electron Microscopy at the Fritz Haber Institute of the Max Planck Society.

More than half a century after the first electron microscope, the technology of microscopy continues to develop and evolve. One major development was the scanning tunneling microscope, invented by Gerd Binnig and Heinrich Rohrer. As the inventors themselves point out, the device permits researchers to "see" complex surface structures atom by atom. The scanning tun-

**Table 4:** Gerd Binnig's and Heinrich Rohrer's most-cited papers from the *SCI*®, 1955-1986. A = number of citations. B = bibliographic data. The *SCI* research front(s) to which the paper is core are included in parentheses.

| A | B |
|---|---|
| 137 | **Binnig G, Rohrer H, Gerber C & Weibel E.** 7 x 7 reconstruction on Si(111) resolved in real space. *Phys. Rev. Lett.* 50:120-3, 1983. (83-2788, 84-2767, 85-1805, 86-1229) |
| 68 | **Binnig G, Rohrer H, Gerber C & Weibel E.** Surface studies by scanning tunneling microscopy. *Phys. Rev. Lett.* 49:57-61, 1982. (83-2788, 84-2767, 85-1805, 86-1229) |
| 67 | **Rohrer H & Thomas H.** Phase transitions in the uniaxial antiferromagnet. *J. Appl. Phys.* 40:1025-7, 1969. |
| 65 | **Rohrer H.** Properties of $GdAlO_3$ near the spin-flop bicritical point. *Phys. Rev. Lett.* 34:1638-41, 1975. |
| 60 | **Binnig G, Rohrer H, Gerber C & Weibel E.** Tunneling through a controllable vacuum gap. *Appl. Phys. Lett.* 40:178-80, 1982. (83-2788, 84-2767, 85-1805) |

**Figure 3:** Historiograph of recent research fronts on technology and applications of electron microscopy. Asterisks (*) indicate research fronts in which Ruska, Rohrer, or Binnig are core authors. Numbers of core/citing papers are indicated at the bottom of each box.



neling microscope can even resolve features that are only about a hundredth the size of an atom.[15] Although jokingly compared by Rohrer to "a rusty nail you drag across a surface,"[16] the device is considerably more complex and has important implications in microelectronics and other fields.

To scan a surface, the scanning tunneling microscope uses a sharp, needlelike probe positioned so close to the sample that the electron clouds of the probe and the sample overlap. Applying a voltage between the tip of the probe and the sample causes electrons to flow through a narrow channel in the electron clouds. This flow is called the tunneling current.[15] Because the density of an electron cloud falls exponentially with distance, the tunneling current is extremely sensitive to the separation between the needle tip and surface. As a result, when the probe scans across the sample, surface features as small as atoms show up as variations in the tunneling current.[17]

According to Binnig and Rohrer, three main design features allow the probe and the sample to interact with such precision. First, the microscope must be entirely shielded from vibrations caused by sound or movement in the immediate environment. Second, the drives of the needle must be very precise. Third, the tip of the probe must be as sharp as the limits of rigidity and stability allow.[15] With their design, Binnig and Rohrer were able to solve experimental difficulties that had thwarted previous researchers in tunneling microscopy. And as the Swedish Academy indicates, the applications of Binnig and Rohrer's device in exploring surface structures have only begun to be seen, in semiconductor physics, microelectronics, chemistry, and other areas.[9] It has already proved instrumental in exploring higher-temperature superconductivity within weeks of the primary discoveries.[18]

Binnig was born in 1947 in Frankfurt and received his PhD in experimental physics at the University of Frankfurt in 1978. He has worked at the IBM Research Laboratory, Zurich, since 1978. Rohrer, born in Buchs, Switzerland, in 1933, received his PhD in physics from the Swiss Federal Institute in 1960 and has worked at IBM in Zurich since 1963.

Table 4 is a list of most-cited papers in which Binnig and Rohrer are coauthors. At the top of the list is a paper from *Physical Review Letters* coauthored with IBM colleagues C. Gerber and E. Weibel, "7 x 7 reconstruction on Si(111) resolved in real space." Cited over 130 times since publication in 1983, it appeared in our study of the most-cited papers in the physical sciences for that year.[19] In fact, in 1983 this paper had already emerged as a core paper to an ISI research front (#83-2788). A 1982 paper, "Surface studies by scanning tunneling microscopy," also from *Physical Review Letters*, was one of the first demonstrations of Binnig and Rohrer's design. This paper has been cited in over 60 publications. It too is a core document to research front #83-2788.

These 2 papers are among the 13 documents that are core to the 1985 research front "Theory and applications of scanning tunneling microscopy," #85-1805. This front is included in the historiograph in Figure 3. Also included is front #85-2288, mentioned previously, which deals with the history and development of electron microscopy. The historiograph demonstrates the variety of ways in which electron microscopy has been applied, including its uses in studying the structures of cells and crystals.

Next week we will conclude our examination of the 1986 Nobel laureates with a discussion of James M. Buchanan, winner of the economics prize, and Wole Soyinka, who won the prize for literature. In the areas of physics and chemistry, the 1986 winners illustrate the immediate and enduring impact of new techniques and technology on scientific research.

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17. **Quate C F.** Vacuum tunneling: a new technique for microscopy. *Phys. Today* 39(8):26-33, 1986.
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