1 → 0) in the magnetic bits beneath. AMR-based heads helped to boost storage density 10-fold.

Using GMR in place of AMR was a clear next step. However, the fields that were needed to switch the magnetization in Fert's and Grünberg's structures were too strong to bring the hoped-for increase in sensitivity. In a series of experiments, a team of IBM researchers including Virgil Speriosu, Stuart Parkin, Bruce Gurney, and Bernard Dieny figured out how to make GMR-based read heads. And in the process, they also elucidated some of the underlying physics.

Unlike Fert and Grünberg, they used sputtering machines to make their multilayers. Even though sputtered layers have more defects than MBE-grown layers, they found GMR in their structures. And because sputtering is faster and cheaper than MBE, they could readily and quickly explore GMR in a wide range of materials and conditions.

Among the key IBM findings is that the all-important spin-dependent scattering occurs mostly at the interfaces between layers, rather than in the layers themselves.

GMR requires ferromagnetic layers to change their alignment with respect to each other. In a GMR-based read head, that is achieved by depositing a layer with low magnetic anisotropy to respond to an external field and to pin the other layer using exchange anisotropy. An important refinement making the pinning strong was the use of two ferromagnetic layers coupled by a ruthenium layer in between. Because the sandwich has low net magnetization, the coupling is enhanced.

Read heads based on this idea (US patent no. 5,159,513) went into production in 1997, just nine years after GMR was discovered. IBM made billions of dollars in sales and licensing.

GMR-based read heads replaced the older AMR-based heads because the two magnetoresistive effects can be realized with similar technology. By 1999 the GMR read head was the industry standard. More than 5 billion of the heads have been produced. Although still in use today, by 2006 GMR read heads were being supplanted by heads based on another MR phenomenon: tunnel magnetoresistance.

TMR was discovered in the early 1970s. Outwardly, the physics is similar. Both GMR and TMR rely on ferromagnetic layers whose band structure features a spin-dependent shift. But in TMR, it's tunneling through an insulator, not scattering in a metal, that provides the magnentoresistance.

TMR had languished because it seemed possible only at impractically low temperature. Then, in 1995, MIT's Jagadeesh Moodera and his collaborators and, independently, Teranobu Miyazaki and Nobuki Tezuka of Tohoku University in Japan saw a GMR-sized effect at room temperature using an aluminum oxide spacer. Nine years later, two groups—one led by Parkin, the other led by Shinji Yuasa of the Nanoelectronics Research Institute in Tsukuba, Japan—replaced aluminum oxide with magnesium oxide and boosted TMR by an order of magnitude. In 2005, Seagate Technology introduced the first drives equipped with TMR read heads.

Although GMR's read-head reign was short-lived, its influence on physics endures, especially in the broader field of spin-based transport or spintronics. Says Prinz, "Albert and Peter really broke open the field."

Charles Day

Albert Fert was born in 1938 in Carcassonne in southwest France. He earned his PhD in 1970 at Université de Paris–Sud in Orsay outside Paris. He remains at UPS, but in 1995 he became the director of a joint venture between CNRS and Thales, the French electronics conglomerate.

Peter Grünberg was born in 1939 in the Czech city of Plzen. He earned his PhD in 1969 at the Technical University of Darmstadt. He started work at the Forschungszentrum Jülich in 1972. Although he officially retired in 2004, he continues to work there part-time.

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Nobel chemistry prize honors career in surface science

Gerhard Ertl's efforts did much to shape the way researchers study surface-catalyzed chemical reactions.

The Royal Swedish Academy of Sciences has awarded this year's Nobel Prize in Chemistry to Gerhard Ertl, professor emeritus and former director of the physical chemistry department at the Fritz Haber Institute of the Max Planck Society in Berlin, Germany, "for his thorough studies of fundamental molecular processes at the gas–solid interface." It's the first time since 1999 that the prize has been awarded for work in physical chemistry, and the first since 1932 that it was awarded for the study of chemical reactions on surfaces.

Ertl was born in 1936 in Bad Cannstatt—now part of Stuttgart—in Germany. His early training in electrochemistry, which deals with chemical processes at the solid–liquid interface, inspired him to start thinking about the chemistry of the solid–gas interface, a nearly unexplored field at the time. At the young age of 31, he became the director of the physical chemistry department at the University of Hanover, taking a similar position at Ludwig–Maximilians University in Munich in 1973 before moving to the Fritz Haber Institute in 1986. His long list of awards includes the 1998 Wolf Prize in Chemistry, which he shared with Gabor Somorjai of the University of California, Berkeley.[1]

A great deal of Ertl's scientific insight involved finding the right tool—or, more usually, combination of tools—for the job. He was always on the lookout for

Ertl

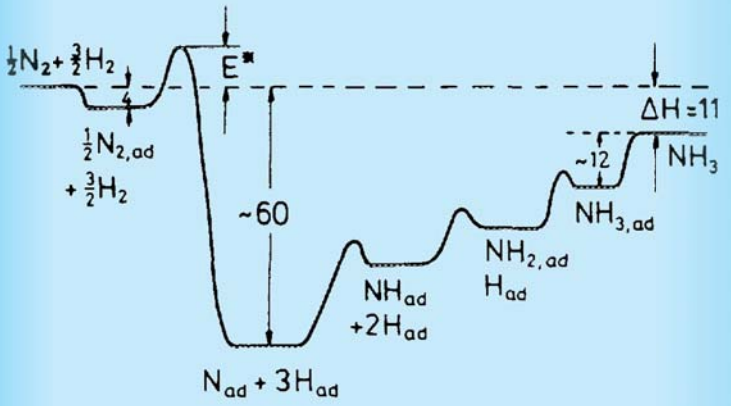

Figure 1. Potential-energy diagram, published by Gerhard Ertl in 1983, of the Haber–Bosch process for surface-catalyzed ammonia synthesis. The subscript "ad" denotes an adsorbed species, and energies are given in kilocalories per mole. The activation energy E^*, which largely determines the rate of the reaction, depends on the particular catalyst used. (From ref. 3.)

new surface-probing methods, based on the various ways that photons and electrons interact with surface atoms; he invited experts on the techniques to come to his lab to teach him and his students how to use them. He built sophisticated ultrahigh-vacuum machines that incorporated several surface probes. And he often returned to important unresolved problems as new techniques became available.

Much of Ertl's early surface-science work involved low-energy electron diffraction (LEED). The physics behind the technique dates back to Clinton Davisson and Lester Germer's famous 1920s experiments, in which they found that slow-moving electrons fired at a crystalline surface were deflected in a diffraction pattern. The interest at the time was in the electron's wave–particle duality; LEED's use as a tool for surface characterization had to wait several more decades. The delay was due in part to the need for better vacuum technology, which was eventually developed in the semiconductor industry.

In the early 1960s, as soon as LEED systems became commercially available, Ertl applied for and obtained funding to buy one. "Before that time," he says, "I had tried to build such an apparatus from glass in my laboratory, myself, but I was not very successful." He recognized that the technique could be used to probe not only the structure of surfaces themselves but also the arrangements of adsorbed atoms and molecules. Since LEED was prone to error resulting from impurities on the surface, Ertl often combined it with other techniques to confirm his results. He always kept an eye toward applications to surface catalysis, the promotion of a chemical reaction by a surface that is not itself used up by the reaction. Surfaces act as catalysts by changing the structures or even breaking the bonds of adsorbed molecules. (See the articles by Ertl and Hans-Joachim Freund, PHYSICS TODAY, January 1999, page 32, and by Somorjai and Jeong Park, October 2007, page 48.)

Haber–Bosch process

Ertl's work on adsorbate structures came to have great practical use in his characterization of the Haber–Bosch process for the synthesis of ammonia, NH_3, from nitrogen and hydrogen. Air is mostly N_2, but it's tricky to get that nitrogen into a chemically reactive form that can be used to make explosives, fertilizer, or other products. The triple bond between two N atoms is one of the strongest of chemical bonds, and few chemical processes can break it.

Developed by Fritz Haber in 1909 and modified to a commercial scale by Carl Bosch and others in 1913, the Haber–Bosch process involves flowing heated N_2 and H_2 (the latter is easily derived from fossil methane) over a mixture of iron and other metals. The process was used for decades, and refined empirically, without anyone fully understanding how it worked. A lingering open question was whether the adsorbed N_2 molecules reacted with hydrogen directly or whether they first dissociated into two N atoms before reacting. Understanding that step was key to designing a way to make the reaction go faster.

In 1974 Ertl attended a conference in Switzerland at which Paul Emmett—a noted researcher on catalysis, and friend and brother-in-law of Linus Pauling—was honored for his 50 years of work on ammonia synthesis. Recalls Ertl, "At the end of the conference, Emmett gave a speech in which he concluded that despite the efforts over so many years, the mechanism is still not clear. That prompted me—I went back to my laboratory and said to my students, 'Let's try this and figure out what's going on.'"

Nitrogen and hydrogen react at a detectable rate only at pressures that preclude the use of Ertl's customary surface probes. But by 1981 Ertl had found a way to probe the high-pressure reaction through low-pressure surface studies.[2] He noticed that at temperatures between 400 K and 600 K, adsorbed N atoms didn't have enough energy to find partners and recombine into N_2 molecules that can desorb from the surface—but all the other molecules involved in the reaction were able to desorb. If he kept the temperature in that range, he could run the reaction at high pressure, pump the reaction chamber down to low pressure, and measure the concentration of N atoms left on the surface.

If the reactive nitrogen species were the N_2 molecules, some N_2 molecules would still dissociate before they had a chance to react. The resulting N atoms would be stuck—they would have no way of leaving the surface through reaction or desorption—so the concentration of N atoms would be large regardless of the H_2 pressure used in the reaction. But Ertl found that the N-atom concentration dropped sharply as he ran the reaction at higher and higher H_2 pressures. In a conclusion he described as "unequivocal," he had found that hydrogen was reacting with N atoms, not N_2 molecules. In other experiments, Ertl elucidated the later steps of the mechanism (see figure 1) by looking at the reverse reaction, starting from ammonia and going backwards.[3]

Carbon monoxide oxidation

One of the most fascinating systems Ertl studied is the surface-catalyzed oxidation of carbon monoxide. Like the Haber–Bosch process, CO oxidation has a practical use: CO is often the product of incomplete combustion of carbon-based fuels—in car engines, for example. It's desirable to convert as much as possible of the poisonous CO to CO_2 by reacting it with oxygen. That reaction is one of the functions of catalytic converters, widely used in automobiles since 1975. Several metals can catalyze the reaction, but platinum exhibits some of the most interesting chemistry and physics. (CO oxidation on the surface of another metal, ruthenium, is discussed in PHYSICS TODAY, October 1999, page 19.)

In principle, the reaction itself is fairly simple. Molecules of CO and O_2 adsorb

on the surface, and each O_2 molecule dissociates into two adsorbed O atoms. An adsorbed CO molecule combines with an adsorbed O atom to form a molecule of CO_2, which immediately leaves the surface. But around 1970 researchers noticed some strange behavior in platinum-catalyzed CO oxidation: The reaction rate oscillated in time. In 1982 Ertl reproduced the oscillations under idealized conditions: a clean, well-defined single-crystal surface under low pressure.[4] He found that the Pt(100) surface made the reaction rate oscillate, but the Pt(111) surface did not.

Ertl's proposed explanation[5] for the oscillations had to do with surface reconstruction, the rearrangement of the atoms on a surface into a structure different from that of the bulk. Many surfaces reconstruct as a way of reducing the strain caused by the reduced coordination of the surface atoms—but an adsorbate covering enough of the surface can undo the reconstruction and restore the bulk structure. In the Pt(100) case, either CO or O can remove the reconstruction, but if they're present together, they react, so in practice a bulk-structure region of the surface is either CO covered or oxygen covered. That makes a total of three structures the Pt(100) surface can adopt: the CO-covered bulk configuration, the oxygen-covered bulk configuration, and the reconstructed configuration. The Pt(111) surface does not reconstruct at all in the 300–600 K temperature range under which the reaction is carried out, which ultimately explains the lack of oscillations on that surface.

The reconstructed surface exhibits a low reactivity because the sticking coefficient for oxygen, a measure of the adsorption probability, is very low. CO can easily adsorb onto the reconstructed surface, but O_2 cannot, so CO accumulates until there is enough of it on the surface to undo the reconstruction. The CO-covered bulk-structure surface also has a low reactivity, but for a different reason. An adsorbed O_2 molecule dissociates immediately, so it requires two adjacent unoccupied sites on the surface; when CO covers so much of the surface, those empty pairs are hard to come by. Occasionally, though—perhaps by chance, or perhaps, as Ertl speculated, due to a surface defect—two adjacent sites do open up, and an O_2 molecule can adsorb. The molecule's two O atoms quickly react with nearby CO molecules, freeing a larger cluster of sites, paving the way for even more O_2 adsorption, and eventually forming an oxygen-covered domain.

The oxygen-covered region is highly reactive because a CO molecule requires only a single isolated surface site to adsorb and quickly react. Keeping the O_2 pressure greater than the CO pressure ensures that O remains the dominant species on the surface, for a while. If, in the course of the reaction, a patch of the surface is cleared of most of its adsorbates, it reconstructs, and O_2 adsorption is inhibited once again. The reconstructed region grows as CO molecules diffuse into the surrounding oxygen-covered areas, and the cycle begins again.

Ertl realized that if he wanted to fully understand the reaction, he needed to measure the surface variations not only in time but also in space. The bulk-structure CO-rich regions could be distinguished from the oxygen-rich regions and the reconstructed regions through LEED or through the photoelectric effect. The work function of the oxygen-covered surface is greater than that of the CO-covered surface, which in turn is greater than the work function of the mostly clean, reconstructed surface. From those experiments Ertl observed the structures moving across the surface in waves (see figure 2a).

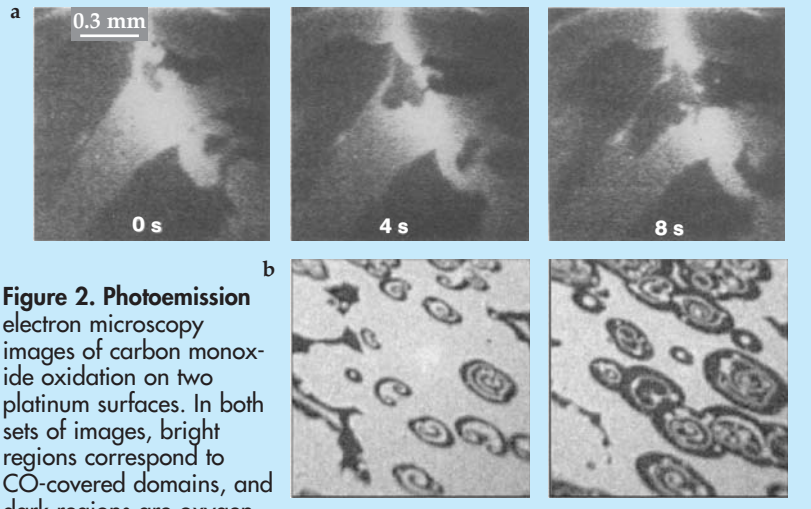

Figure 2. Photoemission electron microscopy images of carbon monoxide oxidation on two platinum surfaces. In both sets of images, bright regions correspond to CO-covered domains, and dark regions are oxygen-covered domains. **(a)** On the Pt(100) surface, the domain boundaries form irregular shapes that propagate slowly across the surface. (Adapted from ref. 8, H. H. Rotermund.) **(b)** On the Pt(110) surface, more complicated patterns form. (Adapted from ref. 9.)

Pattern formation

In 1986 Ertl observed kinetic oscillations in the CO-oxidation reaction on the Pt(110) surface but found that they differed in many ways from those on the Pt(100) surface.[6] Because the Pt(100) structures propagated across the surface by diffusion, there wasn't a high degree of correlation among distant parts of the surface, so the oscillations never formed quite the same shape twice. The Pt(110) oscillations, on the other hand, were regular and reproducible. The Pt(100) oscillations had periods of several minutes, but the Pt(110) oscillations took just a few seconds. The changing structures on the Pt(100) surface could be tracked by LEED, but LEED studies of the reaction on the Pt(110) surface initially got nowhere. And whereas the Pt(100) system could be made to oscillate over wide ranges of temperature, O_2 pressure, and CO pressure, a small change in any of those three parameters was enough to knock the Pt(110) system out of the oscillatory regime.

The main cause of the differing behavior is the extent to which O_2 adsorption is suppressed on the reconstructed surface. On the reconstructed Pt(100) surface, the O_2 sticking probability is so small that it can be ignored completely. But in the Pt(110) system, the O_2 sticking probabilities on the bulk-structure and reconstructed surfaces differ by less than a factor of 2. Since the likelihood of O_2 adsorption still decreases overall with increasing CO coverage, there's a much smaller range of conditions under which the greater sticking probability on the bulk-structure surface has any effect. As a result, the Pt(110) system is much more sensitive than the Pt(100) system to the reactant pressures; that sensitivity can explain why the Pt(110) reaction rate oscillates so rapidly.

As the system cycles through the states of varying reactivity, the reactant pressures change. In the Pt(100) system, the changes in pressure (on the order of 1%) aren't enough to noticeably affect the reaction, but in the much more sensitive Pt(110) system, they are. And since pres-

sure waves in the gas phase propagate much more quickly than do diffusion waves of adsorbed molecules, a change in one region of the surface has an almost immediate effect on the reaction in other regions. As a result, even distant points on the surface can behave in a highly correlated way, and the reaction rate oscillates quickly, regularly, and reproducibly.

With a pressure-mediated mechanism postulated,[7] Ertl set out to image the Pt(110) surface during the reaction. He turned to photoemission electron microscopy (PEEM), a technique that measures the spatial and temporal variation in the surface work function. The photoelectrons from the entire surface are passed through a cathode lens to create images in real time, with much better time resolution than is possible using techniques that involve scanning the surface—just what Ertl needed to study the fast oscillations on the Pt(110) surface.

Originating in the early days of electron microscopy in the 1930s, PEEM later fell out of favor as transmission electron microscopy and scanning electron microscopy proved more suitable for most problems of interest. In the late 1980s, the Fritz Haber Institute's Wilfried Engel developed a PEEM apparatus, optimized for studying surface reactions such as CO oxidation, that could easily be added onto Ertl's ultrahigh-vacuum apparatus.

The results were surprising. Instead of the slow diffusion waves and irregular shapes on the Pt(100) surface, Ertl saw spirals (see figure 2b), bull's-eye patterns, synchronized standing waves, and rapidly changing chaotic shapes, depending on the reaction parameters.[8] More recent work by Ertl and his colleagues has involved controlling the reaction in the chaotic regime by creating a feedback loop between the integrated PEEM intensity and the CO pressure[9] (see also PHYSICS TODAY, July 2001, page 18).

Handling the pressure

Like many other surface techniques, PEEM works only at low pressure. But kinetic studies revealed evidence of qualitative differences in the CO reaction at low pressure and at high pressure: At low pressure, the oxygen atoms stay on the surface of the Pt crystal, but at high pressure some of them penetrate beneath the surface to form a Pt oxide. And the reaction rate at low pressure is slow enough that the heat generated by the exothermic reaction dissipates quickly enough that the temperature remains constant, but at high pressure significant temperature differences build up between regions of low and high reactivity, and those temperature differences in turn affect the reaction rate.

Imaging the surface under pressures higher than about 10^{-3} torr requires a technique that probes the surface with photons only. One suitable technique is ellipsomicroscopy, which measures spatial variations in the change in polarization of light reflected from the surface. The CO-covered and oxygen-covered surfaces change the polarization in different ways, due to their unequal dielectric properties. Harm Hinrich Rotermund, then head of the Fritz Haber Institute's surface imaging group and now at Dalhousie University in Canada, worked on the technique, with Ertl's guidance. Recalls Rotermund, "The day we saw our first spirals with ellipsomicroscopy he left an important visitor in the hands of his secretaries and rushed downstairs to the lab to witness our final success. His curiosity in science has always been his first priority."

Johanna Miller

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New experiments fuel debate over the nature of high-T_c superconductors

A central issue is whether an observed energy gap seen above the critical temperature T_c is related to or different from the superconducting gap seen below T_c.

The parents of the copper oxide high-temperature superconductors are antiferromagnetic insulators. It's thought that they would conduct electricity were it not for the very strong interactions among their electrons. Just dope those insulators to a level of 5% or more by chemically adding or removing electrons, and you get the cuprate compounds that superconduct at critical temperatures T_c up to 140 K. When T_c is plotted as a function of doping, it encloses a dome-shaped superconducting region, as seen in figure 1a. Abutting the dome on the low-doping side is a mysterious "pseudogap" region, in which materials exhibit a gap in the density of states near the Fermi energy even though they are not superconducting. Theorists seeking the mechanism underlying high-T_c superconductors must account for the strongly interacting parents and the pseudogap neighbors.

The plot in figure 1a has two temperature scales: T_c, the temperature at which electrical resistance drops to zero, and the strikingly high T^*, above which the pseudogap disappears. A heated debate has raged for years concerning the significance of the two temperature scales.[1] Do they imply the existence of two different phenomena, each characterized by a distinct energy gap? Or is the pseudogap an extension of the superconducting gap?

The two-gap scenario is consistent with a class of theories holding that competing orders vie for dominance in the copper oxide compounds, one ordered state being a superconductor and the other something like a spin or charge density wave. In such theories, the pseudogap is associated with the competing order and may be essentially different from the superconducting gap. Another class of theories favors a one-gap scenario, in which the two temperature scales are part of the same phenomenon, with electron pairs forming at the higher temperature T^* but not condensing into coherent, superconducting pairs until the temperature drops to T_c. Two temperature scales are seen, for example, in antiferromagnetic materials such as manganese oxide: The magnetic moments develop at a high temperature and order at a much lower one. By contrast, conventional superconductors are characterized by only one temperature, T_c, at which pairs both form and condense.