

(Laboratoire d'Electronique et Physique Appliqué, Limeil-Brevannes),<sup>5</sup> and by Alex Ignatiev, Franco Jona (both at Stony Brook), Jepsen and Marcus,<sup>6</sup> among others.

In a typical LEED study, a monoenergetic electron beam impinges on a crystal surface that is at a pressure no greater than  $10^{-9}$  torr. The periodic structure of the solid surface diffracts the electrons into discrete beams that form a pattern of spots on a hemispherical fluorescent screen. From the distribution of spots, the periodicity of the structure—the symmetry and arrangement of a unit surface cell—is determined directly.

Plotting the spot intensity as it varies with the energy of the incident electron, the experimenter determines the intensity profile or LEED spectrum. These intensity profiles are the raw data from which theorists must determine the atomic structure of the surface; that is, the positions of the atoms within the surface cell. The LEED studies are generally done along with others, such as Auger spectroscopy, to identify the surface atoms present.

As early as 1930, Philip Morse had analyzed LEED intensity profiles and realized that multiple scattering occurred. This is in contrast to x-ray scattering: Because x rays are scattered only once, a relatively simple kinematic (characterized by a single scattering) analysis of x-ray diffraction is sufficient. Over the years, theorists tried to analyze LEED intensities with modified kinematic models. In 1964, Geoffrey Gafner (National Physical Research Laboratory, Pretoria) showed<sup>7</sup> the need for a dynamical (that is, multiple scattering) theory, and two years later K. Hirabayashi and Y. Takeishi (Toboshiba Electric Co.) worked out<sup>8</sup> a first-order approximation to a dynamical approach. That same year Eion McRae (Bell Labs, Murray Hill) reported<sup>9</sup> a multiple-scattering dynamical model that was an exact treatment of a model applicable to LEED.

In his paper, McRae recognized the importance of inelastic collisions and of the details of the atomic scattering potentials but did not develop these points. Realistic atomic scattering potentials were developed by several theorists, culminating in the work of Pendry and Andersson<sup>10</sup> and of Jepsen, Marcus and Jona.<sup>11</sup> John Beeby (Harwell, UK) had in 1968 described<sup>12</sup> a general theoretical treatment of the scattering problem. In 1969 Duke and Charles Tucker (General Electric, Schenectady), who extended<sup>13</sup> the purely elastic analysis of Beeby, and, independently, Robert O. Jones and John Strozier (both then at Cornell), described<sup>14</sup> treatments of inelastic collisions that predicted reflectivity maxi-

ma for clean metals to be of the order  $10^{-2}$  to  $10^{-1}$ , the same as observed maxima. Models that neglect damping give maxima of order unity.

The Beeby-Duke-Tucker model, as extended by Duke and Laramore, finds the same structure from a given set of data as does the McRae model, as extended by Pendry and Andersson and by Jepsen, Marcus and Jona. In other words there are now several theories and computer programs that will give the same structure from the same data.

Among the first surface structures to be worked on—with varying degrees of success—were aluminum, copper, nickel, beryllium, silver, gold, palladium, tungsten, graphite, lithium fluoride, sodium chloride and lead selenide.

Andersson and Pendry reported the first successful overlayer calculation by a multiple-scattering method. They studied sodium on a nickel (100) surface, and assumed a  $C(2 \times 2)$  layer of sodium on nickel; that is, the sodium atoms lie above the fourfold-symmetric hollows in the nickel substrate with two nickel atoms below for each sodium atom in the overlayer. They found a Na-Ni interlayer distance of about  $2.9 \pm 0.1$  Å.

Forstmann, Berndt and Büttner used Pendry's method to locate iodine on silver (111). Their result of 2.8 Å for the Ag-I bond distance, is the same as the interatomic distance measured in AgI crystals.

Several groups have recently reported work on overlayers on nickel. At IBM, Demuth, Jepsen and Marcus, using the data of Demuth and Thor Rhodin (Cornell), calculated the structure of chalcogens (oxygen, sulfur, selenium and tellurium) on nickel (001). Andersson, Pendry, Kasemo and Van Hove studied oxygen on nickel (001) and found an interlayer distance of  $1.5 \pm 0.1$  Å. The IBM group found an oxygen nickel interlayer distance of  $0.90 \pm 0.1$  Å. Duke, Lipari, Laramore and Theeten found a sulfur-nickel interlayer distance of  $1.70 \pm 0.1$  Å for nickel (001) whereas the IBM group found  $1.30 \pm 0.1$  Å for sulfur on nickel (001).

There is no agreement yet on the reasons for these discrepancies. Duke feels that comparing sets of LEED data is difficult because experimenters may use different incident energies and angles to form overlayers. The IBM group, however, does not think that these differences in interlayer spacing are due solely to the small discrepancies in the experimental data used by different groups. Marcus told us they find that, although several different displacements may provide moderate agreement with theory, only one displacement gives agreement comparable to that achieved for the clean surface. Rhodin notes that among the possibil-

ities is that the differences in experimental data being analyzed may actually be due to differences in the structure being studied; these structures may not have been formed under exactly equivalent conditions. McRae suggests that the problem may also lie in the details of the atomic scattering potentials.

How closely do these studies relate to chemical reactions at surfaces? The low-energy electron diffraction work leads to the structure of ordered surfaces, which can be related to theories of chemical bonding. However, the study of chemical reactions at surfaces requires more information because such reactions probably take place at surface defects. One recent effort in this direction is the work of Gabor Somorjai (Berkeley) who has been studying<sup>15</sup> chemical reactions on stepped surfaces of crystals.

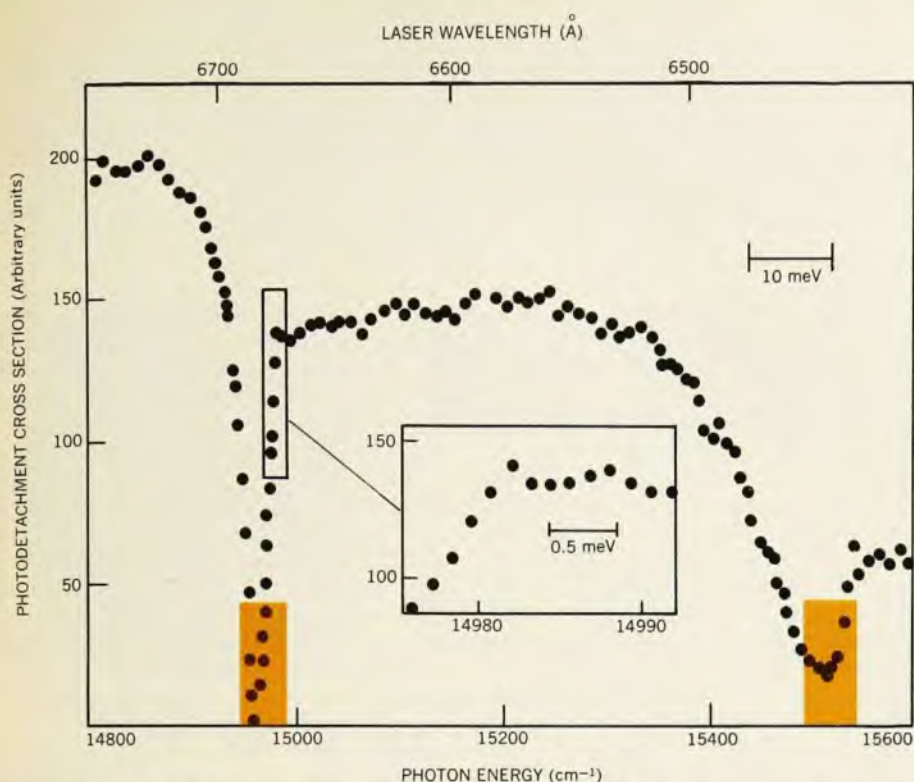
—Marian S. Rothenberg

## References

1. S. Andersson, J. B. Pendry, *J. Phys. C*, **6**, 601 (1973).
2. F. Forstmann, W. Berndt, P. Büttner, *Phys. Rev. Lett.* **30**, 17 (1973).
3. J. Demuth, D. W. Jepsen, P. Marcus, *Phys. Rev. Lett.* **31**, 540 (1973).
4. S. Andersson, J. B. Pendry, B. Kasemo, M. Van Hove, *Phys. Rev. Lett.* **31**, 595 (1973).
5. C. B. Duke, N. O. Lipari, G. B. Laramore, J. B. Theeten, *Solid State Comm.* **13**, 579 (1973).
6. A. Ignatiev, F. Jona, D. W. Jepsen, P. Marcus, *Surf. Sci.* **40**, 439 (1973).
7. G. Gafner, *Phys. Sci.* **2**, 534 (1964).
8. K. Hirabayashi, Y. Takeishi, *Surface Sci.* **4**, 160 (1966).
9. E. G. McRae, *J. Chem. Phys.* **45**, 3258 (1966).
10. S. Andersson, J. Pendry, *J. Phys. C* **5**, L41 (1972).
11. D. W. Jepsen, P. M. Marcus, F. Jona, *Phys. Rev. D* **5**, 3933 (1972).
12. J. L. Beeby, *J. Phys. C*, **1**, 82 (1968).
13. C. B. Duke, C. W. Tucker, *Surface Sci.* **15**, 231 (1969).
14. R. O. Jones, J. A. Strozier, *Phys. Rev. Lett.* **22**, 1186 (1969).
15. B. Lang, R. W. Joyner, G. Somorjai, *J. Catalysis* **27**, 405 (1972); S. L. Bernasek, G. Somorjai, *Phys. Rev. Lett.* **30**, 1202 (1973).

## Narrow resonances seen in alkali photodetachment

While making the first accurate experimental determinations of the electron affinities of alkali negative ions, a team at the Joint Institute for Laboratory Astrophysics (of the University of Colorado and the National Bureau of Standards, Boulder) has stumbled upon what appears to be by far the narrowest resonance observed in any electron-atom



**Cesium negative-ion photodetachment cross section**, showing the two resonances observed near the opening of the  $^2P_{1/2}$  channel (on the left) and the  $^2P_{3/2}$  channel (on the right) in the neutral cesium atom. In the inset the data near the  $^2P_{1/2}$  channel opening are displayed on an expanded energy scale. The energies of electrons photodetached from the negative ions can be measured independently by photoelectron spectroscopy; the electron-energy peaks (colored areas) coincide within experimental accuracy with the opening of the  $^2P$  channels. (Redrawn from T. A. Patterson et al., *Phys. Rev. Lett.* **32**, 189, 1974.)

scattering process. Tom Patterson, Hartmut Hotop, Abe Kasdan, David Norcross and Carl Lineberger report their work with lithium, sodium, potassium, rubidium and cesium negative ions in the 4 February issue of *Physical Review Letters*. As well as giving the electron affinities for these ions the JILA team shows cross-section curves for the photodetachment process that include strong resonances, as narrow as 150 microelectron volts (FWHM) in the case of rubidium. These resonances, not predicted by previously existing theoretical work, occur near photon energies corresponding to the formation of the neutral atom in its first excited ( $^2P$ ) state. The JILA group, an unusual collaboration of theoretical and experimental specialists working on the same problems, also reports improved calculations for these scattering processes that show theoretically how the resonances arise.

The electron affinity of an atom is the binding energy of an added electron—or the energy that must be supplied to detach this electron from the corresponding negative ion. Although in some ways analogous to the ionization potential of a neutral atom, electron affinity is much harder to measure; the energies involved are quite small and negative ions are not easily made in copious quantities. Thanks to recent

improvements in negative-ion sources and the ready availability of laser light sources, however, workers at JILA have in recent years been able to make photodetachment studies and electron-affinity measurements for elements such as copper, silver, gold, platinum, selenium and sulfur.

Resonances in atomic collision cross sections caused great excitement when they were discovered about a decade ago. First predicted theoretically (for elastic scattering of electrons in atomic hydrogen) by Phil Burke and H. M. Schey in 1962, resonances were first observed in the lab by George Schulz of Yale in 1963. Since then many resonances (or “compound states,” or “temporary negative ions”) have been identified in electron-impact cross sections for both atomic and molecular systems; Schulz has reviewed the data in two papers in the July 1973 issue of *Reviews of Modern Physics*. Most of these resonances are so narrow (of the order 50 meV) that they could not be resolved in electron-collision experiments before the development of electrostatic electron-energy analyzers (or “monochromators”) during the 1960’s.

The JILA group has two independent techniques for measuring electron affinities, and both were applied to the recent alkali-atom work. In one, called “photoelectron spectroscopy,” a nega-

tive-ion beam crosses the beam of a 4880 Å argon-ion laser within the laser cavity and the energies of the photodetached electrons are analyzed in a hemispherical electron-energy analyzer. The difference between the photon energy and the energy of the slow electrons gives the electron affinity. The other technique involves direct measurements of photodetachment cross sections as a function of laser wavelength; for these measurements the negative-ion beam interacts with photons from a tunable dye laser, neutral atoms and negative ions are separated and the neutrals detected on a secondary-emission detector. In principle, the onset of the photodetachment cross section would be a direct measure of the electron affinity. In practice, however, this energy (for alkalis) is outside the range currently available from dye lasers, and it is the onset of photodetachment into excited states of the neutral that is observed. Provided the excited channel can be unambiguously identified, subtraction of the excitation energy for that level gives the electron affinity.

The figure shows the photodetachment cross section plotted against photon energy for cesium in the energy range that includes the opening of the  $^2P_{1/2}$  and  $^2P_{3/2}$  channels in the neutral atom. Also shown are the data from the photoelectron spectroscopy experiment; electron-energy peaks for the  $^2P_{1/2}$  and  $^2P_{3/2}$  processes coincide, within experimental uncertainty, with the opening of these channels in the cross-section curve.

Immediately below each of these channel openings lie the unexpected resonances. Near the  $^2P_{1/2}$  threshold the cross section goes to zero, and the resonance there is about 1 meV wide (FWHM). The equivalent resonance in rubidium is even narrower, about 150 microelectron volts, as measured with a laser linewidth of about 0.15 Å.

Norcross, working originally with David Moores (now returned to University College London), has investigated these collisions with close-coupling calculations to see if the resonances have a theoretical basis. With a three-state approximation (6s-6p-5f), he shows that autoionizing states in the continuum just below each component of the first excited state of the neutral atom produce a very sharp dip in the cross section—not detected in earlier, two-state, calculations. So far he cannot reproduce the drop of at least  $10^3$  that the experiments show in cesium, but he believes this is due to a lack of convergence in the calculations.

The JILA group intends to continue their investigations for other two-electron atoms, including some they have examined in the past, to see if corresponding resonances above higher excited states can be detected. —JTS