Role of crystallography

Contemporary crystallographic techniques for examining the structures of solids and their excitations and defects use generators ranging from new miniature x-ray tubes to synchrotrons and pulsed-neutron sources.

Sidney C. Abrahams and Jerome B. Cohen

Fundamental advances in materials research depend heavily on crystallographic information. Modern crystallography is concerned with the structural topology of the various states of order in matter; in particular, with the atomic arrangement, collective excitations, and electron and defect distributions in solids. The crystallographic techniques of importance to materials research cover a wide range; an overview was published recently.[1]

The introduction, in the last decade, of very intense sources of both x rays and neutrons, of a new group of x-ray detectors, the advances in electron microscopy and the use of automation have greatly increased the scope of many of these techniques, and have stimulated the development of new ones. Crystallography was among the first sciences to introduce automation, and now the minicomputer is a component of many crystallographic laboratories.

In this article we will highlight some instrumental aspects of contemporary crystallography and their role in materials science, including powder profile fitting, energy-dispersive and x-ray-flash diffractometry, and x-ray and neutron scattering techniques. The implications of possible future developments, such as the miniature x-ray tube, will be sketched. A considerable impact on the materials industry is likely from the portable crystallographic tools now being developed for nondestructive testing. At the other extreme is the "self-destructive" experiment shown in figure 1, in which an explosive charge sends a shock wave through a material while x-ray diffraction data are collected.

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Automated diffractometry

Precise knowledge of the atomic arrangement of a material is a prerequisite to understanding its properties. The determination of crystal structure requires accurately measured integrated intensities of the Bragg reflections. Sets of these data are usually taken from single crystals of the material. The measurement, now customarily made on a computer-controlled diffractometer, uses either x rays or neutrons with wavelengths on the order of 10^{-10} m. Such an automatic diffractometer is capable of systematically searching a predetermined volume of reciprocal space and, from the angles at which diffraction maxima are recorded, indexing the reflections. A crystal of unknown composition is mounted on a diffractometer and the unit cell can be determined—within a few hours in favorable cases—with an accuracy of about 0.005 Å. A set of 1000–2000 integrated intensities can be measured and reduced to structure factors in one or two days. Computer programs supplied with automated diffractometers aid in solving and refining the crystal structure.[2]

However, the full benefits of automatic diffractometry are often not obtained immediately with crystals of interest to materials research: Mechanical and electrical twinning and other disorders must first be eliminated, or allowances made; failure to do so can result in misleading or uninterpretable results. For example, investigation of ferroelectric or ferroelastic crystals requires initial depoling (coalescing a number of antiparallel electric domains into a single domain) or detwinning experiments to eliminate later ambiguities. Most advances in ferroelastic materials have followed initial crystallographic investigation, often by automated single-crystal diffractometry. Figure 2 shows how a compressive stress changes the x-ray diffraction profile of a ferroelastically twinned crystal of platinum germanium selenide.

Modern automated powder diffractometry is on the verge of providing considerable support for materials development and quality control, as the diffraction pattern can be measured and stored in the memory of a controlling minicomputer and then compared with a library of over 26 000 known patterns for identification.

Angle-dispersive powder patterns by neutron or x-ray diffraction were, until recently, usable in structure analysis only if enough diffraction lines were sufficiently well resolved to give the integrated intensities of more reflections than the number of variables in the structure. If this condition were not met, the pattern was generally of value only as a means of identification. In two approaches, developed to better use the information contained in a powder pattern,

- a structural model is fitted to the pattern, and
- the entire pattern is represented by a series of convolutions.

Hugo Rietveld[3] initiated the former approach in 1967 by fitting many points on the profile of a neutron powder pattern to calculated ones from a model, which can be refined by the method of least squares. This is possible because the individual peak profiles obtained with a neutron beam from a reactor have a known (gaussian) form. In an experiment the intensities of all points in the powder-diffraction pattern are measured at small intervals, such as 0.1°, over a wide range of scattering angle. Many materi-

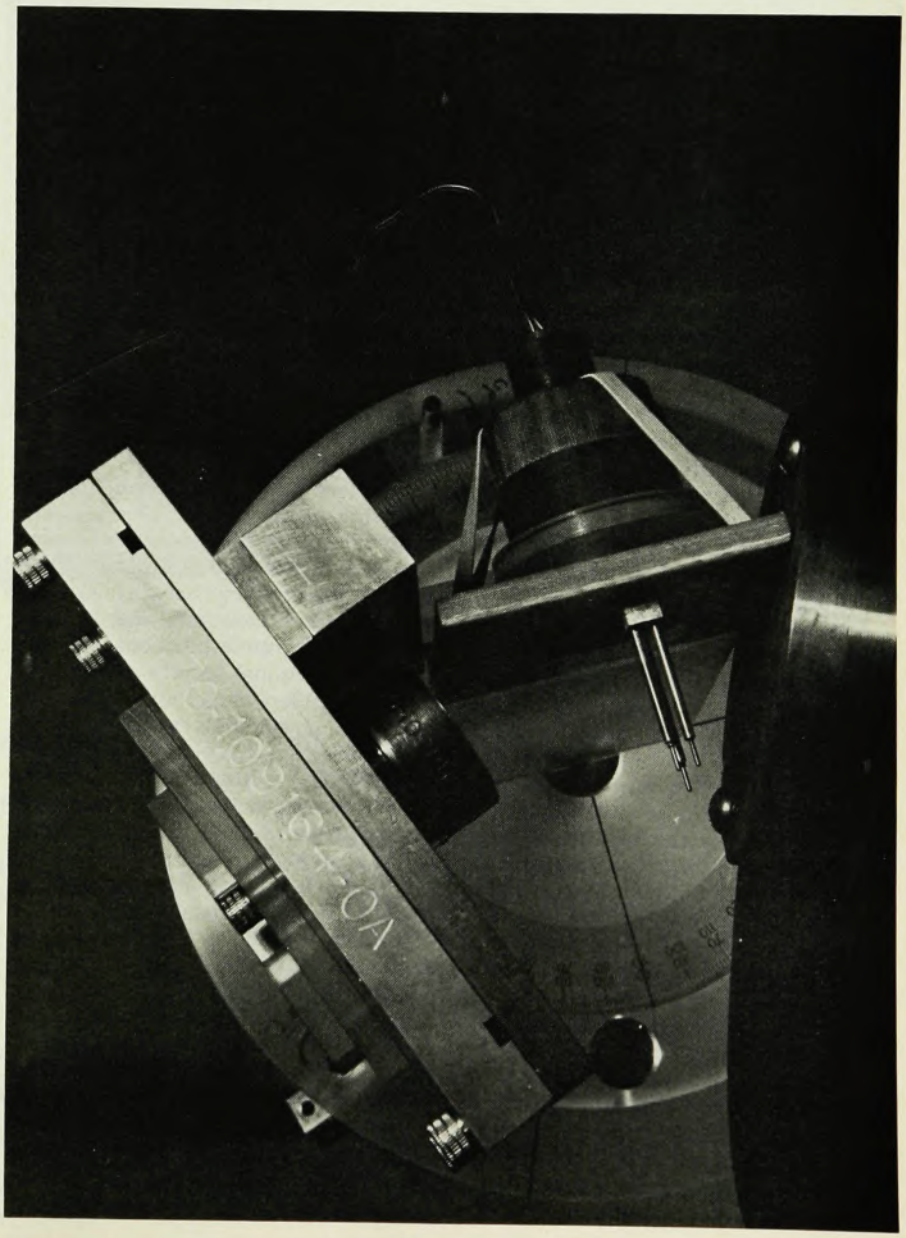
als that form twins or can not be grown as single crystals are amenable to structural analysis by this method. A recent example is the determination of the nuclear and magnetic structure of $Sr_2Fe_2O_5$ by Brian Fender and others at Oxford.

The structural fitting approach has been extended very recently to x-ray powder patterns by Ray Young of Georgia Tech.

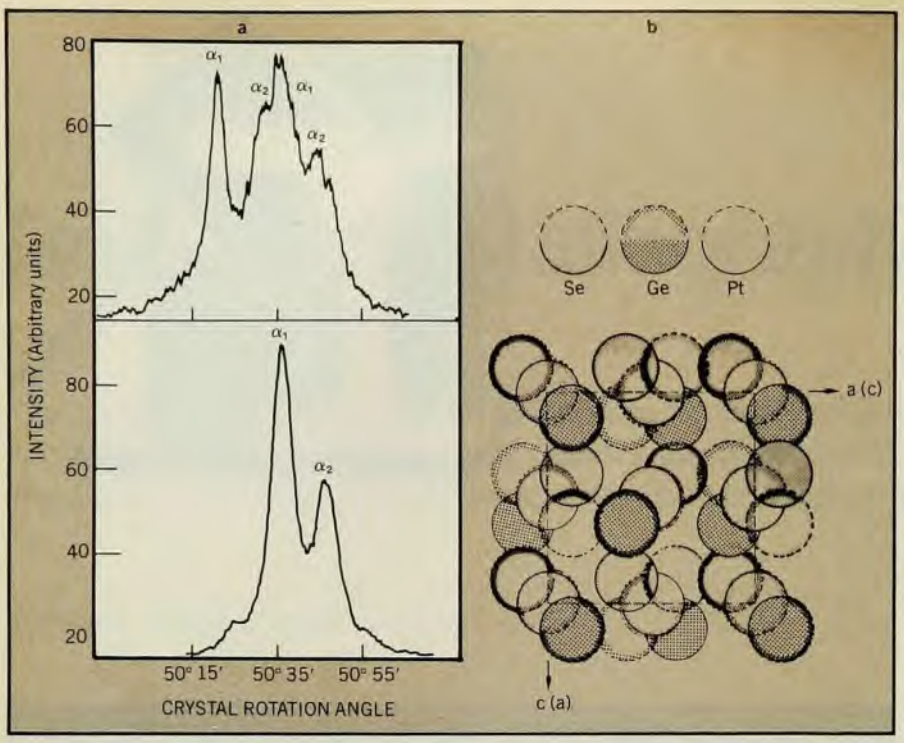
The second, deconvolution, approach was developed for x-ray powder diffractometry and energy spectroscopy by William Parrish and his collaborators at IBM. They simulated the experimental profile by the convolution of three functions, each composed of several lorentzians, together with a background. Overlapping peaks are resolved by this method if their angular separations are greater than one fifth the full peak width at half height. An example of the method is the resolution for Cu Kα radiation of 144 Kα_1 and Kα_2 peaks in a topaz powder pattern with angle 2θ between 92° and 147°, which required an associated computational time for fitting of about 1 minute. Of these, 48 peaks were previously unresolved.

Data at extreme conditions

In energy-dispersive diffractometry, continuous radiation from an x-ray tube is used in combination with solid-state detectors of doped or intrinsic germanium or silicon having good energy resolution



Flash x-ray diffraction experiment seen from above. The device with wires is the high explosive, the camera is on the left and the plastic diffractometer stand is shown below. The x-ray source, not visible in the photo, is off to the right. The technique has shown that some materials undergo a phase transformation during the shockwave compression. Photograph courtesy of Quentin Johnson of Lawrence Livermore Laboratory. Figure 1



X-ray diffraction profiles of reflection from a ferroelastically twinned crystal of platinum germanium selenide (a, top) and from the same crystal surface following the application of a compressive stress of 14 MN/m^2 (a, bottom). The lower profile shows that the Cu Kα_1 and α_2 components are now resolved. The atomic arrangement of PtGeSe is shown in b. Whereas the twinned crystal contains atoms in positions corresponding to both solid and dashed circles, the untwinned crystal (with the *a* axis horizontal) has atoms at the solid outlines only. (After S. C. Abrahams, J. L. Bernstein, E. Buehler, Mat. Res. Bull. **11**, 70; 1976.) Figure 2

for x rays (for example, 140 eV at 5.9 keV). This technique is complementary, with a separate range of useful properties, to the more usual methods of angle-dispersive diffractometry. The usual experiments involve a *constant wavelength* and variation of the angle made by the specimen with the beam; different crystal planes diffract at different angles. With energy dispersion, many planes diffract at one *fixed angle* by selecting the proper wavelength from the continuous incident spectrum.

Energy-dispersive methods are capable of determining lattice constants from powder specimens with a precision of about 10^{-4}, and both single-crystal and powder intensities with an accuracy of about 5%. By selecting an appropriate angle we can make measurements at wavelengths selected for an advantageous energy to enhance anomalous scattering effects.[4] This is illustrated in figure 3 for the determination of polarity in a single crystal of gallium phosphide. As the following paragraphs indicate, energy dispersion is useful for studying the properties of materials under unusual conditions, in which it is most convenient for the direct and diffracted beams to be confined to fixed paths. In combination with a conventional goniometer, an energy-dispersive detector allows simultaneous measurement of both diffraction patterns and spectrographic data. Such combinations offer the promise, in some instances, of greatly simplified multiphase analysis for materials research. An important problem is the determination of the composition, thickness and orientation of thin films. Energy-dispersive detectors have been used successfully for such work, with film thicknesses on the order of 10^{-7} m.

The properties of materials often of most interest are those at pressures and temperatures far from normal. Crystallographic instrumentation is now available for investigating changes in symmetry and lattice constants and, in some laboratories, atomic positions and collective excitational spectra over a wide range of pressure and temperature. Microcrystalline materials can be studied by x-ray diffraction with either photographic recording or photon-counter diffractometry at pressures at high as 500 kbar and temperatures to 1200 K, with the diamond-anvil high pressure cell developed by Stanley Block and others at the National Bureau of Standards; this work is described in detail in an article in the September 1976 issue of PHYSICS TODAY. Modified diamond-anvil cells have been used to study single crystals of several materials at 50 kbar on an x-ray diffractometer. Absorption of the direct and diffracted x-ray beams by the high-pressure cell results in greater problems for x-ray than for neutron diffractometry, although the former has the advantage of accepting much smaller specimens.

Neutron-diffraction data on powders were obtained by Denis McWhan (Bell Labs) at 43 kbar with an alumina Bridgman-type cell. Single-crystal and powder neutron measurements at pressures to 10 kbar are commonplace. Christian Vettier and others at Grenoble also used an alumina cell for neutron diffractometry, studying a single crystal at 40 kbar in the liquid-helium temperature range. A modification, recently made with McWhan, is expected to allow both pressure and temperature to be varied continuously throughout this range.

Instrumentation for single-crystal x-ray diffractometry is now readily available for temperatures down to about 20 K for samples at atmospheric pressure. Ralph Simmons of Illinois University reached 0.03 K with a He^3–He^4 refrigerator. X-ray powder diffractometry of samples at temperatures in the liquid-helium range is widely available, and neutron diffractometry of single crystals or powders at those temperatures has been a standard technique for many years.[5]

Several high-temperature single-crystal diffractometers have been built; they operate to about 1700 K.

X-ray flash diffraction

Intense pulses of characteristic x rays as short as 40 nsec can be produced from Blumlein-type devices. Quentin Johnson of Lawrence Livermore Lab developed[6] a technique using such a device to probe single crystals as they undergo shock-wave compression, producing shock pressures as high as 300 kbar. The technique allows x-ray-diffraction measurement of the shock-transformed material at the instant of transformation. With a "self-destructive" experimental arrangement such as that shown in figure 1, several materials have been shown to transform to the hydrostatically compressed state essentially as single crystals, and others to undergo a phase transformation during the shockwave compression. It is expected that x-ray flash diffraction will be extended to study many nonequilibrium systems, including important short-lived intermediate (that is, metastable) structures.

We will also mention several important areas in x-ray spectroscopy,[7] although these are not universally regarded as part of crystallography. Trace elements can now be determined by measuring fluorescent radiation to a precision of about 5–10%, with a detection limit of about 10^{-6}. The use of high-efficiency air-cooled miniature x-ray tubes[8] only one third the size of conventional x-ray tubes, with a minicomputer for the mathematical techniques needed to analyze the spectra, results in equipment quite modest in size. Solid-state detectors allow many fluorescence peaks to be detected at one incident angle, and are now often added to scanning electron microscopes for *in situ* chemical analysis. It is possi-

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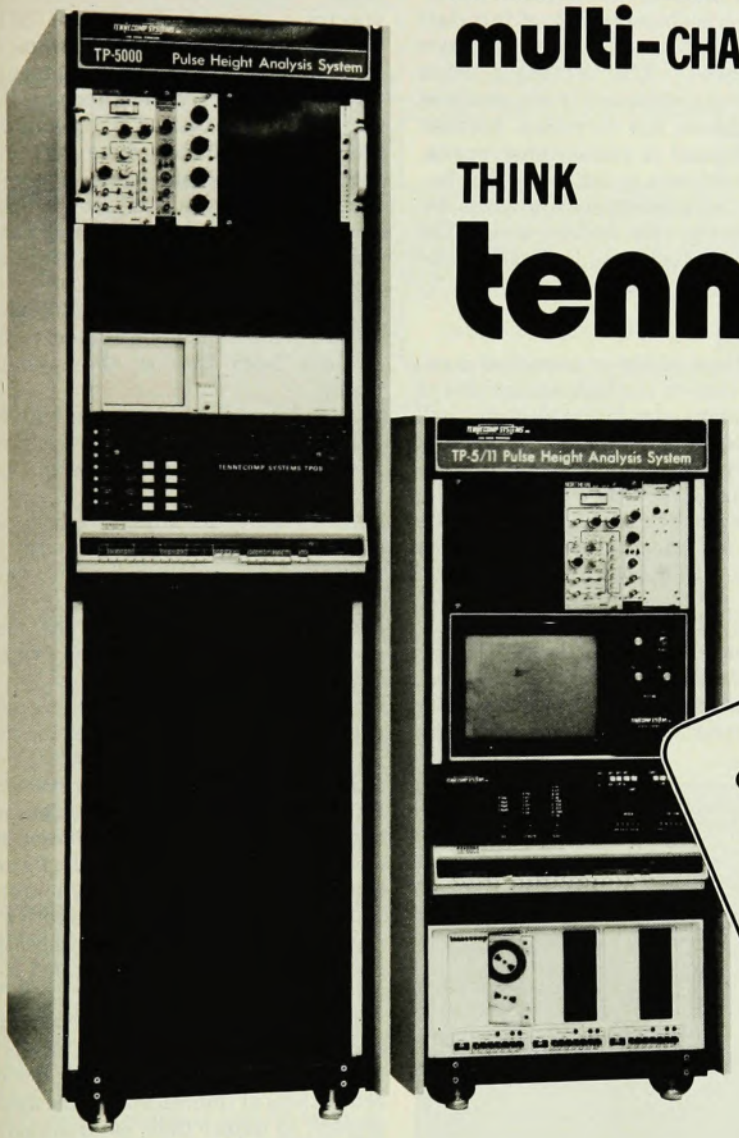

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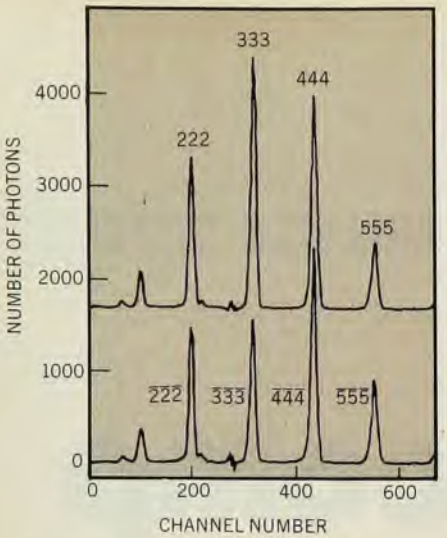


The relative intensities of *h h h* and $\bar{h}\,\bar{h}\,\bar{h}$ reflections, obtained from a single crystal of gallium phosphide by energy-dispersive diffractometry, allow rapid determination of the crystal's polarity. (After S. Hosoya, T. Fukamachi, in reference 4, page 203.) Figure 3

ble to form an image with the secondary electrons or fluorescent x rays so that the spatial distribution of the elements in small specific regions can be examined.

Numerous techniques related to the various electron transitions associated with fluorescence (generally produced by incident electrons, soft x rays or ultraviolet light) have been established, including

- photoelectron emission,
- x-ray emission,
- x-ray absorption, and
- Auger-electron emission.

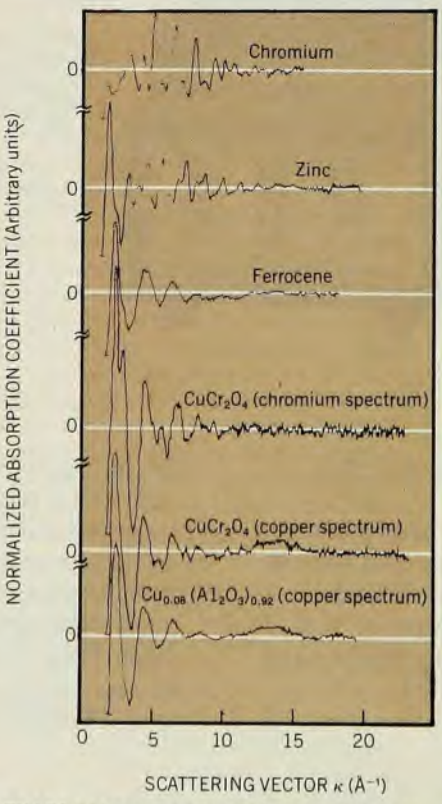
The range in solids of ejected electrons is much less than that of fluorescing x rays, so the ejected electrons are very useful for surface analysis.

New detectors allow Mössbauer spectra to be obtained in back reflection from bulk specimens, instead of in transmission through thin foils—the usual technique. A gas-filled detector with the specimen forming the window and a fine-mesh grid to reduce field distortions was developed by Jon Spijkerman, then at the National Bureau of Standards. The resonant absorption of gamma rays by iron is accompanied by the decay of the excited nucleus through emission of gamma rays or by K-electron capture. In the latter case the energy transmitted to the electron exceeds the binding energy, and the escaping electrons can be detected. For either process, the efficiency of the detector is adjusted by changing the gas in the detector.

Whereas electrons escape from a depth of 0.3 microns in iron, gamma rays emerge from depths of 25–30 microns, allowing both the bulk and the surface of the sample to be examined nondestructively. In a quenched 1095 steel, for example, Lyle Schwartz and his co-workers at Northwestern University found that the amount of retained austenite on the surface is half that in the bulk. Thomas Cranshaw of Harwell found that some normally austenitic stainless steels, in particular those more susceptible to corrosion than is characteristic of this class of material, appear to have a surface layer of martensite. The technique offers many new possibilities for the study of wear, oxidation and corrosion, because these all depend on surface phenomena. Surface roughness is not important because the measurements are made by backscattering; this feature makes the instrument valuable in production situations.

EXAFS

Oscillations in the transmitted x-ray intensity close to the high-energy side of the absorption edge for an electron shell of a given atom are called "EXAFS," which stands for "extended x-ray absorption fine structure." Interpretation is not completely clear very close to the edge, but the effects there appear to be associated with many-body interactions, distortion of the excited-state wave function by the Coulomb field of the excited atom, and with band effects. However, oscillations about 30–1000 eV from the edge are largely associated with the scattering of the wave field of the ejected electron by neighboring atoms.



EXAFS spectra for body-centered-cubic chromium, hexagonal zinc and other crystals. The example of Cr and Cu in $CuCr_2O_4$ shows that two different elements in a compound, with different environments, produce different EXAFS. (After F. Lytle and others, Boeing.) Figure 4

Interference between these scattered wave fields gives rise to patterns similar to radial-distribution patterns but with the advantage that the distribution is around a specific and known (fluorescent) atom.[9] This is illustrated by the EXAFS spectra in Figure 4. Because of the high scattering cross section of electrons, considerable theoretical development of multiple-scattering phenomena will undoubtedly be necessary for quantitative analysis, but already some very interesting qualitative information on materials has been provided by Edward Stern, Farrel Lytle and their co-workers at the University of Washington and at Boeing, and by other groups:

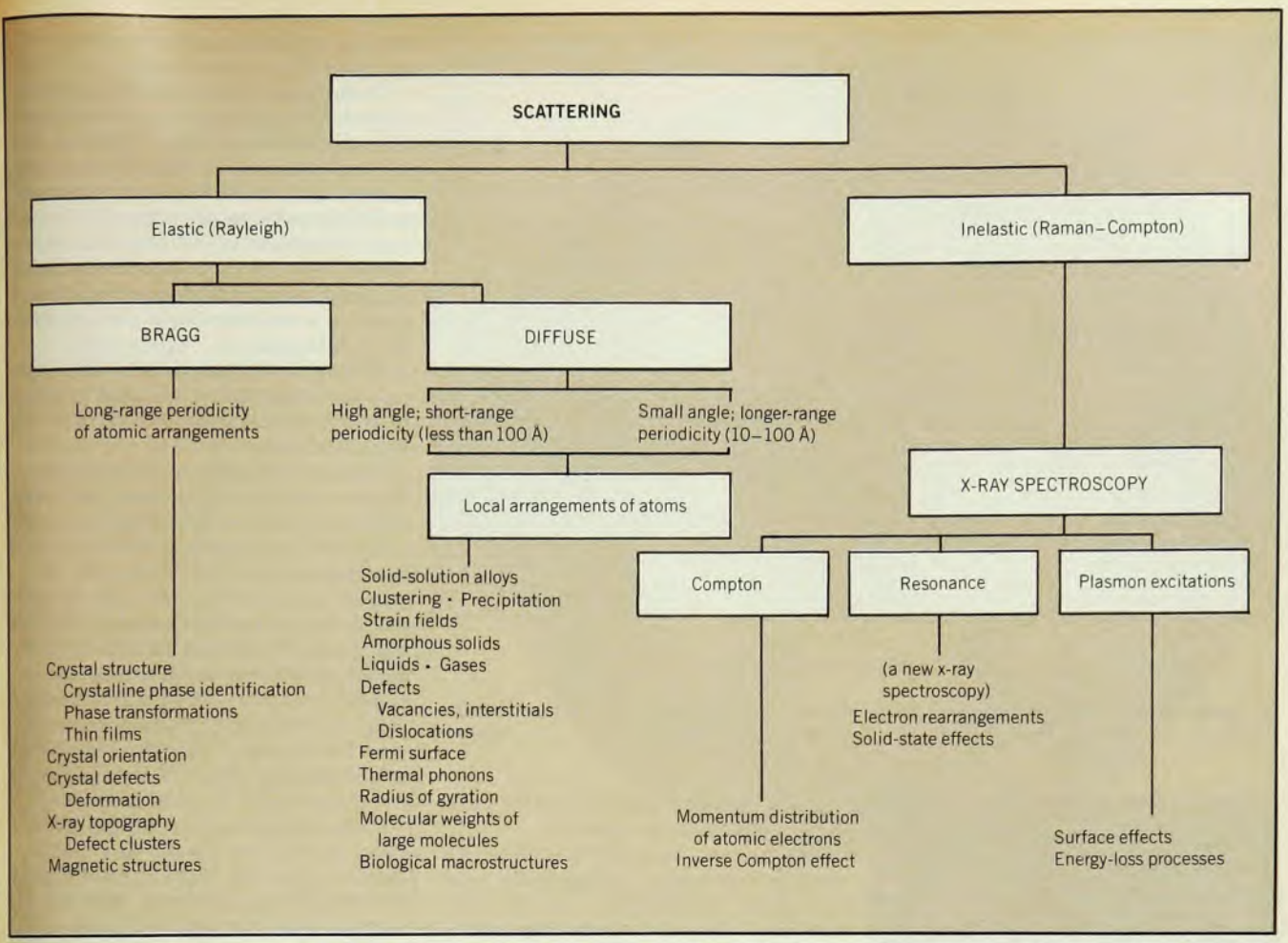
- In amorphous GeO_2, the environment about a germanium atom is found to differ strongly from that in the crystalline forms.
- In gold and platinum catalysts supported on Al_2O_3, the gold atoms have at least two different near-neighbor environments.
- In copper–chromium catalysts supported on Al_2O_3, copper is in a tetrahedrally coordinated environment whereas the chromium is in octahedrally coordinated sites, forming a spinel. The valence of the chromium changes after exposure to automobile exhausts.

The EXAFS technique requires measurement only of the transmitted x-ray intensity as a function of energy through a thin specimen. The energy is selected by varying the angle of a monochromator crystal, by using the white radiation from an x-ray tube or, more recently, by using synchrotron radiation. Synchrotron sources have become available with x-ray fluxes about 10^5 times more intense than the bremsstrahlung from sealed x-ray tubes.

Detailed studies of the effects of exposure to various poisons on catalysts are now possible. Since only very low concentrations of fluorescent atoms need be present to detect their environments, a wide range of new material studies is possible on the role of minor constituents in alloys, ceramics and polymers. The new high-intensity x-ray sources discussed below will further expedite such studies.

New ideas in x-ray scattering

Numerous interactions between x radiation and matter exist that provide important materials information,[10] as illustrated by figure 5. Rotating-anode x-ray generators are now commercially available that yield fluxes 10–100 times more intense than those from sealed x-ray tubes. Linear and area position-sensitive detectors based on large arrays of elements (up to 256 × 256) or on multiwire proportional drift chambers have average counting-rate capabilities up to 1 MHz. Simultaneous detection of large parts of the diffraction pattern reduces measure-



Basic x-ray scattering interactions, indicating the experimental techniques from which the various types of information about the spatial arrangement of atoms and molecules listed can be obtained. (From Sparks, Oak Ridge National Laboratory.) Figure 5

ment time by an additional one to two orders of magnitude.

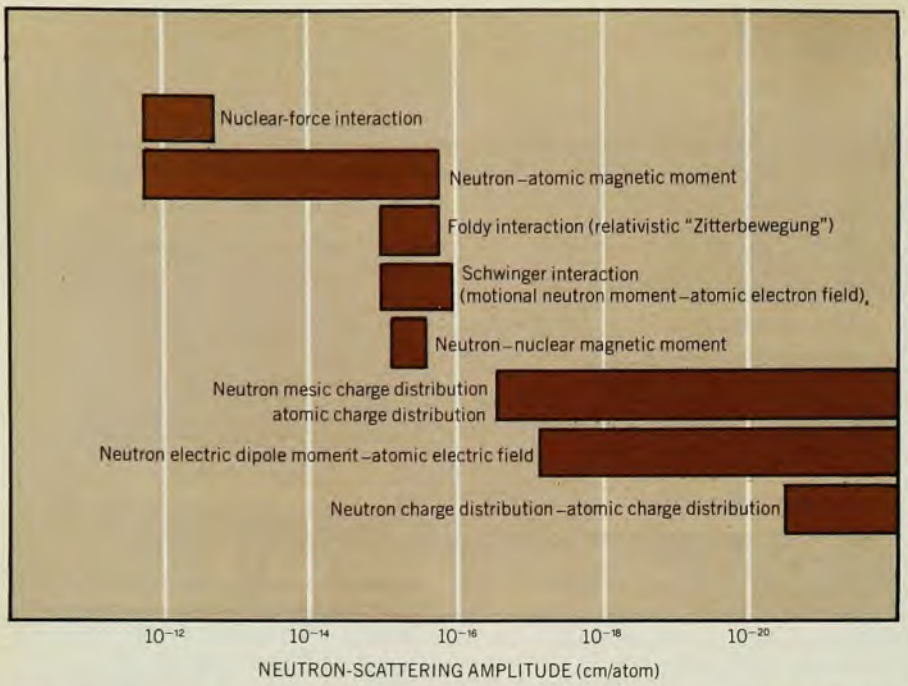
The value of the combination of increased x-ray intensity with modern detectors is illustrated by H. G. Haubold's (Jülich) measurements on electron-irradiated aluminum[11] with a point-defect fraction of about 10^{-4}. Haubold used a 100-kW x-ray generator and an array of 100 detectors. In spite of Compton and thermal diffuse scattering about 100 times greater than the diffuse scattering from the defects, Haubold detected the intensity from interstitials "split" along the [100] direction, with an interstitial and a displaced atom forming a dumbbell along [100]; other possible locations or configurations were unambiguously excluded.

Similar studies on dilute concentrations of alloying elements with attendant distortions are possible, and some are under way. Stephen Sass of Cornell used a 12-kW x-ray source to give photographs of diffraction patterns from single grain boundaries; he estimates that a third of a monolayer of gold on a surface is detectible. Robert Hendricks of Oak Ridge National Laboratory has built a small-angle system 10 m long with such a high-intensity x-ray generator and a two-dimensional position-sensitive detector. As an example of its use, size distributions of voids in accelerator-irradiated specimens are being studied. Similar work by electron microscopy is extremely tedious. Hendricks feels that this system rivals anything that can be done at the moment with a synchrotron in terms of angular resolution and signal-to-noise ratio. It appears possible that, with higher-power sources such as synchrotron radiation, and with position-sensitive detectors, the surface structures, including surface contamination, wear, corrosion and small particle structure (catalysts), might be studied with less complication than with the electron techniques now largely used.

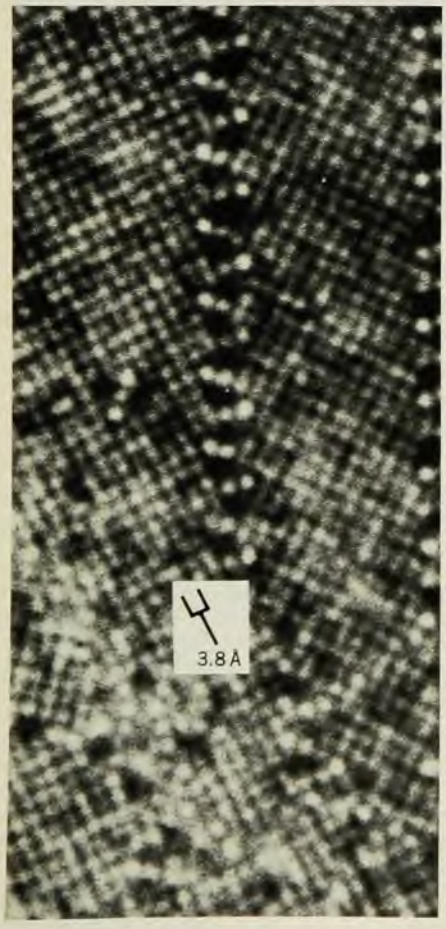
An interaction of x rays with the magnetic moment of an atom has been detected by Erwin Bertaut's group at Grenoble.[12] Although the interaction is weak, the use of total reflection to eliminate half-wavelength scattering allows us to record with a normal x-ray tube, in only a matter of hours, a magnetic reflection from an antiferromagnet. The more intense sources now available should permit the study of magnetic materials by many laboratories without convenient access to neutron scattering facilities.

Residual stress may now be measured by diffraction methods *in situ* by using linear position-sensitive detectors that accept a diffraction pattern extending over an angle θ of 10° with computer-controlled systems developed by Cohen and by R. Barbier of C. G. R. (France) and Charles Ruud of the Denver Research Institute. Use of the miniature x-ray tube will extend such techniques to one-person portable units, which will allow field measurement of the stresses that influence mechanical behavior in rails, bridges, pipelines, crankshafts and so on, in under a minute.

Among the unique features of synchrotron x radiation is the wavelength range, 0.3–1000 Å, available with high intensity. Small-angle x-ray scattering can be performed with sufficient intensity at long enough wavelength that crystalline reflections can not occur, thus eliminating multiple scattering, a source of difficulty only avoided hitherto by employing neutrons of such long wavelength that Bragg reflection is not allowed. The small-angle scattering experiments will facilitate study of clustering in alloys and the rheology of polymers. Other features of synchrotron x radiation are the narrow divergence (about 0.1°), plane polarization and narrow source width which, together with the high intensity, are most valuable for studies of highly perfect crystals. Because synchrotron sources



The basic interactions of neutrons with atoms, showing ranges of the corresponding scattering amplitudes. (After C. G. Shull, Trans. Amer. Cryst. Assoc. **3**, 1; 1967.) Figure 6



High-resolution electron micrograph of a crystal of $4Nb_2O_5{\cdot}9WO_3$, showing the nucleation of a disordered tetragonal tungsten-bronze-type structure at twin boundaries of the near-cubic WO_3-type phase; large white spots are pentagonal tunnels. (Photograph by S. Iijima, Arizona State University.) Figure 7

are pulsed, the possibility exists for a new type of dynamic experiment.

Synchrotron sources have also been used for high-resolution, high-speed x-ray diffraction topography of large single crystals: Exposure times for photographic recording are typically reduced to seconds from the several hours required with conventional x-ray sources. Electronic detection results in a further reduction to the order of milliseconds for the exposure, permitting topographic study during phenomena such as crystal growth, plastic deformation and corrosion. The most generally useful synchrotron source of x radiation presently available in the United States is the SPEAR storage ring at Stanford. Upgrading this facility and creating a new dedicated national synchrotron source would immensely benefit our crystallographic and other scientific programs.

Neutron scattering

Eight different types of neutron interactions with atoms are known, covering a range of more than 16 orders of magnitude in scattering intensity, as illustrated in figure 6. Neutron scattering is particularly valuable for materials research in view of the following:

- The ratio of neutron scattering for various elements is often quite different from that of x-ray scattering. Hydrogen and other light atoms may thus be more readily detected, as well as some anions in ceramics.
- Orientations and magnitudes of magnetic spins can be determined.
- Neutrons can exchange energy with phonons in a solid by inelastic scattering, so that the phonon spectrum and diffusive motions are more readily examined with neutrons than with x rays.

Changes in phonon spectra preceding several kinds of phase transitions have been studied increasingly. Although it is still not clear exactly what causes phase changes in any specific case, their nature is becoming better understood. Among other important experiments now being undertaken are small-angle-scattering studies of vacancy clustering in alloys and changes in polymer-chain configuration during deformation. Studies of isotopically substituted polymers confirm that polymer chains coil in the bulk in many plastics, a finding previously only inferred from other data.

Short-wavelength neutrons have been used to study chain-segment motion in polymers, showing that there is no impedance to such motion in the bulk, in contrast to the situation when the polymer is in a solvent. Studies of such properties as viscosity have also indicated this result. With the new high-intensity sources it is now possible to examine materials such as rubbers, where pinning along the chain offers resistance to motion even in the bulk. This effect, important in understanding such materials, can not be studied easily by other methods.

Adsorbed gaseous species on solids are being probed by elastic and inelastic neutron scattering. New scattering peaks are sometimes associated with the arrangement of the adsorbed species, and the vibrational spectra of the gas before and after adsorption reveals information about the bonding.

Nuclear reactors such as those at Oak Ridge, Brookhaven or Grenoble have thermal fluxes of about 10^{15} neutrons $cm^{-2}\,sec^{-1}$. Higher neutron intensities are obtainable by bombarding a heavy-atom target with pulsed high-energy protons from an accelerator and moderating the emitted neutrons. Peak fluxes of 10^{17} neutrons $cm^{-2}\,sec^{-1}$ at 60 Hz are feasible with a pulsed neutron source having a much lower background than that of a thermal reactor. Scattering techniques differ for pulsed neutron sources as reciprocal space must be explored in *all* experiments by energy analysis of the scattered polychromatic neutron beam.

Pulsed sources are under construction in some countries. A proposal to construct a pulsed-neutron source in the US has not been funded yet, delaying its availability for at least 5–6 years. (Similarly, US nuclear centers are seriously in need of upgrading to continue competing successfully with other countries in understanding the solid state.) Pulsed-neutron sources, with their attendant high flux of short-wavelength neutrons, enable measurements to be made to much higher wavevectors than at present, allowing the structure and interatomic forces in amorphous solids, for example, to be more clearly unravelled. However, many pro-

cesses, such as long-range fluctuations in liquids and fast ionic conductors, magnetic materials, relaxations in polymers and optical modes in some solids can not be explored with present sources. This is due to the required combination of high energy exchange with the neutron beam and low momentum transfer, which is not achievable with thermal neutrons. An added advantage of a pulsed neutron source is a reduction in the size of the sample that can be employed.

Electron microscopy and diffraction

Transmission electron microscopy (TEM) has undergone three major developments in the last decade: Diffraction patterns can now be obtained from areas as small as 30 Å in diameter and chemical analysis made from regions as small as 250 Å in diameter, for example by Roy Geiss of IBM. The extent of strain contrast is reduced, and hence more closely spaced defects are seen, by imaging in dark field with the "side" of a Bragg peak, the so-called "weak-beam method" devised by David Cockayne of Sydney University. With correct defocussing and specimen alignment, images can be obtained that show the arrangement of atomic groups within the unit cells of many oxides and minerals, revealing clearly both the ordered structures and the detailed forms of crystal defects. Figure 7 is an example, taken by Sumio Iijima, in John Cowley's group at Arizona State.

Convergent-beam or bend-extinction contour patterns can lead to determinations of symmetry and changes in lattice constants over small regions with an accuracy of about 10^{-4}, as illustrated in figure 8. Characteristic changes occur in electron diffraction patterns from relatively thick crystals at accelerating voltages greater than about 100 kV. Information on the outer-atomic-electron redistribution, the composition and long-range order in alloys, interstitials in oxides, and atomic static or thermal displacements can sometimes be obtained from these critical voltages.

The scanning electron microscope (SEM) has also become a widely used tool in materials research.[13] A focussed electron beam is scanned across the specimen as in a TV camera and a selected part of the transmitted or reflected beam is accelerated to a detector and then displayed on a cathode-ray tube. The SEM has a much greater depth of field than the optical microscope for equivalent resolution and a much greater range of useful magnification, and so provides a valuable extension of the capabilities for the study of surfaces. It has found applications in many scientific and technological areas, including the imaging and testing of solid-state circuitry. Figure 9, an SEM photograph by M. Meshii and collaborators, shows grain boundaries at a titanium surface.

Convergent beam pattern from silicon [111] zone axis, taken with 200-kV electrons, reveals a mesh of higher-order K lines (Kikuchi in electron, Kossel in x-ray, diffraction) of fine angular diameter. (After G. M. Rackham and J. W. Steeds of Bristol University.) Figure 8

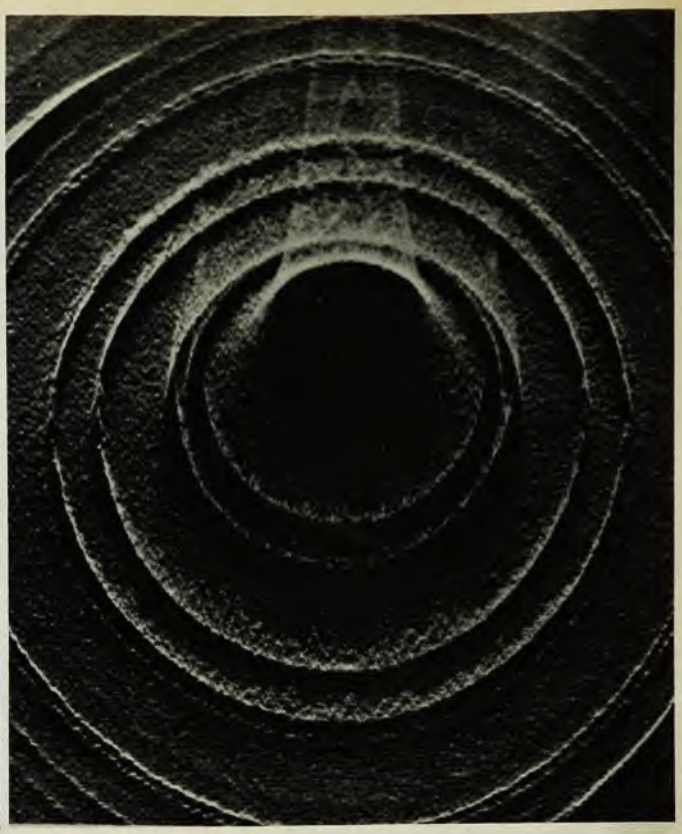
The scanning transmission electron microscope has many advantages over the conventional TEM for ultrahigh-resolution studies of single atoms and molecules. Resolution has not yet reached the stage, however, at which individual atoms can be seen in most crystalline solids. For thick specimens, resolution and penetration may be somewhat better because there are no imaging lenses after the specimen, and therefore less chromatic-aberration effects associated with the large energy spread of inelastically scattered electrons. Also, the image signal can be detected with greater efficiency and, because it is detected electronically rather than on a fluorescent screen or photographic plate, it can be manipulated very effectively to improve contrast or to permit image analysis and processing.

Scanning electron diffraction with energy discrimination is emerging as a valuable technique in which the usual photographic steps are replaced by electronic techniques. Transmission scanning and scanning transmission electron diffraction are techniques made readily available by modification of conventional 100-kV electron microscopes. The former technique was used by Dennis Maher of Bell Labs to take the brightness-modulated diffraction pattern of a polycrystalline aluminum film shown in figure 10. These are techniques that allow the very fine regions, previously mentioned, to be examined.

The resolution of TEM's now available increases significantly up to 500–700 kV and then levels off because of mechanical and electrical instabilities. A resolution of 2 Å has already been achieved with a 500-kV instrument in Japan; when a resolution of about 1.7 Å is reached it should be possible to "see" individual atoms even in the closely spaced arrays of simple metals and semiconductors. Even higher voltages are desirable for examination of thicker specimens: A limit of about 5 microns is imposed by degradation of the image caused by chromatic aberration. At these thicknesses, however, deformation studies are more like those in the bulk and the sources and sinks of point defects at the surfaces become less important.

High-voltage scanning instruments are also of interest because of their possibly better resolution and flexibility as compared to TEM's for very thick specimens. The high-voltage scanning transmission electron microscope built by Marija Strojnik at Arizona State has shown a penetration, at 500 kV, equivalent to a 1.2-MeV conventional TEM; but it is smaller, cheaper and more easily housed.

The surface of titanium, shown at a magnification of about 1000 in this scanning electron micrograph, reveals its grain boundaries. The specimen was thermally etched. Because of its great depth of field and range of magnifications, the SEM technique has many applications. (After M. Meshii and others, Northwestern University.) Figure 9



Three-dimensional diffraction pattern of an aluminum film about 100 Å thick. The brightness-modulated photograph, obtained by scanning 100-kV electrons transmitted through the film, shows high spatial and angular resolution. (After D. M. Maher, *Scanning Electron Microscopy,* part 1, IIT Res. Inst., Chicago, 1974.) Figure 10

Albert Crewe of the University of Chicago is trying to develop a 1-MeV instrument with 1-Å resolution. A national facility, or funding, for developing techniques, theory and equipment in this field would greatly benefit materials research.

The structure of surfaces in high vacua are now studied primarily by electron-diffraction techniques:

- In reflection high-energy electron diffraction (RHEED), the electrons are accelerated through a range 10–100 kV and both surface layers and the bulk or substrate are sampled, together with the interaction between the scattering from both.
- In low-energy electron diffraction, the electrons are accelerated only to the 5–500 V range and only the first few surface layers are sampled.[14]

Recently, surface structures studied in high vacua have increasingly been analyzed with multiple-probe techniques, either sequentially or simultaneously, because these combined methods provide enhanced information. Both clean crystal surfaces and adsorbed layers have been studied extensively. Kenneth Matysik of Bell Labs, for example, uses RHEED, mass spectrometry and molecular-beam techniques together for the simultaneous determination of structural aspects, thermodynamics and nucleation kinetics with surface coverages ranging from submonolayers to thick deposits.

Seeing atoms in solids

Modern technology is so heavily dependent on materials research that many future plans depend on successful solutions to current materials problems. Enormous contributions to the understanding of materials already have been made by the broad field of crystallography. These were made first in the area of basic structures; then in understanding imperfections, lattice vibrations and magnetic-moment distributions. We are now entering a new regime that promises to bring us closer to literally seeing atoms in real solids and to understanding surface reactions, phase transformations and cooperative atomic motions. A fuller commitment to funding the newer techniques is urgently needed in the United States. We also need a strengthening of crystallography in the materials departments of our universities, to provide an adequate number of specialists to utilize fully, or even comprehend, the expected advances.

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