

Analytic Characterization of MATERIALS

Organized at the behest of ARPA and attended by some 75 representatives of more than 20 universities, government laboratories, and industrial organizations concerned with programs in materials research, the Symposium on the Analytical Characterization of Materials was held January 20-21 at the RCA Laboratories in Princeton. J. Kurshan is manager of RCA's Research Services Laboratory.

By J. Kurshan

At a recent meeting on crystal growth and defect characterization, there were many researchers who expressed a need for more and better facilities for analytical work. To help fulfill this need, Charles F. Yost, director for materials science, Advanced Research Projects Agency, proposed that a symposium be arranged to present, in a consolidated fashion, the capabilities and limitations of available analytical resources, especially as they relate to materials problems in ARPA-sponsored laboratories. The ensuing symposium, organized and held at RCA Laboratories was conducted in the spirit of a workshop or "clinic" with ample opportunity provided for discussion. There was an informality that resulted in considerable audience participation and interaction. The talks and discussions covered not only technical aspects of particular analytical procedures, but also the over-all problem of effectively coupling analytical service to a materials research program.

Materials researchers acknowledged that it is costly and sometimes impossible to try to make progress without adequate analysis. Analysis plays an especially critical role in the more difficult problems which involve a large investment of effort. It was stressed that the value derived from an analytical facility depends not only on the available people and techniques, but also on the quality of communication that is established between user and supplier in their day-to-day working relationships. The symposium helped to bring analysts and materials researchers together in candid discussion.

The analysts present were agreeably surprised at the praise sent their way. Too often the acknowledgment of their work is little more than a polite "thank you". There is a real problem in providing adequate recognition of the contribution that analysts make to the successful outcome

of the research. There is also a problem in generating a positive attitude among materials researchers toward supporting the other needs of the analyst—money, space, and equipment. Support is also needed for the research that must be done to extend analytical methods.

The demands placed on the analyst are for more and more determinations to be made to part-per-million and even part-per-billion sensitivity. Equipment is now available to fill such demands. However, as brought out in this meeting, the main need today is for improved accuracy (as distinguished from precision) at these low concentration levels. Improved standards, in turn, are basic to achieving and maintaining this accuracy. It was also emphasized that more sensitive methods put more stringent requirements on homogeneity of the standard and its reliability when used in small amounts. In addition, the analysis of microregions is becoming ever more important for two reasons: first, we are learning how defects on a microscale affect the characteristics of materials; second, materials are being used to make microminiature devices that have intentionally varied composition and structure on a microscale. Electronic instrumentation has already made one revolution in analysis by providing sensitive and accurate detection devices. A second revolution is on the way using scanning and display techniques to probe microregions.

C. F. Yost (ARPA) presented introductory remarks emphasizing that improved electronic materials are a foundation stone of much recent technological growth. Limited knowledge of materials restricts the functions that can be designed into a given system. The national importance of research on materials has been recognized and advanced by the current ARPA program which took five years of organizational effort. It em-

phasizes improvement of purification and crystal-growth techniques, acquisition of well-defined crystals, and precise characterization of crystals. Enunciating the applications significance of materials research results was stressed as a problem of all those engaged in the program, not just the people in the government agencies.

H. W. Leverenz (RCA) put analysis in perspective in the normal sequence of events that a new material goes through: concept, purification, synthesis, crystallization, analysis for composition and structure, measurement, interpretation, evaluation, and application. Years ago the people involved were usually the same ones at each stage, with good communication, but poor efficiency. Today, there are specialists with greater efficiency at each stage, but poorer communication and feedback. A major problem that exists is to improve the coupling among these individual specialists. L. R. Weisberg (RCA) discussed analysis from the viewpoint of a practicing materials-research man. He pointed out that this meeting was novel in presenting the role of analysis in its direct relation to materials research. The appreciation of materials researchers for analysis came slowly over a long period of time, as he illustrated by several examples. Going back to the early days of germanium purification, it took about two years to find out that many of the annealing effects that were attributed to vacancies were instead due to copper contamination. In the case of silicon, oxygen concentrations at the level of 100 parts per million went undetected for a couple of years. With GaAs, proper analytical results changed the entire course of a research project on purification. Once silicon was identified as the offending impurity, it was traced to the quartz crucibles used in growing the GaAs crystals, and the program shifted to finding a more suitable crucible material. Modern instrumentation, such as the solids mass spectrograph, would have simplified the analytical problem and hence shortened the research time by at least a man-year of effort.

R. Roy (Pennsylvania State University) analyzed in chart form the total characterization that might be appropriate to a newly synthesized material. He pointed out that one should be aware of the complete description that is possible, and then relax the requirements in specific cases as appropriate. The critical information is that which is needed to describe the material sufficiently so that someone else can reproduce it. In addition to characterizing the material by composition, structure, imperfections, phases, etc., Roy emphasized that it is also necessary to understand the ther-

modynamics of the system which may not be in equilibrium. Concerning trace analysis, W. W. Meinke (National Bureau of Standards) emphasized that high-purity materials are more characteristic of the impurities than of the materials themselves. Consequently, the analyst must be at the forefront of absolute measurements and standardization in the materials field. Meinke listed five key problems that are common to trace analyses regardless of the origin of the problems: speed, contamination, standards, sampling, and accuracy.

Members of the RCA Laboratories' Materials Analysis Group presented an integrated series of talks on the operation of a *centralized* analytical facility supporting a research program on materials which are of electronic interest. These activities were presented in terms of the basic analytical methods employed, using actual materials problems as illustrations. S. J. Adler described the development of the organization and the facilities of the group as an evolutionary process of adapting continually in response to actual analytical problems presented for solution. Thus, emphasis has been placed here in developing analytical methods and equipment of very general and broad applicability. A natural division exists in the analysis of materials between composition and structure (including habit and morphology). Full characterization of a material requires information in both categories. The methods used for the first category include wet chemical analysis in order to determine macrocomposition; spectrophotometry for concentrations of dopants; emission spectrography for macrocomposition, dopants, and impurities; mass spectrography and neutron activation for trace impurities; x-ray fluorescence for macrocomposition and dopants; and radioisotope tracing for distribution of impurities. For structure determination the following were used: x-ray diffraction (both Laue and Debye-Scherrer), electron microscopy and diffraction, light microscopy, microradiography, and Coulter counting.

It often appears that instrumental methods have all but taken the chemistry out of chemical analysis. K. L. Cheng brought the story up to date for wet chemical analysis and described how new techniques have reduced the time required for chemical analysis. Wet chemical methods are especially useful where high accuracy is needed in the determination of major constituents or impurities present in microgram or larger amounts. Accuracies of two or three percent are typically obtained and with special effort, accuracies better than 0.1 percent are possible. The application of newly developed complexing agents such as

ethylenediaminetetraacetic acid (EDTA) has streamlined the classical wet chemical-analysis techniques. More than 90 percent of all elements can be directly or indirectly titrated with EDTA, the platinum metals being notable exceptions. The use of masking and demasking techniques increases the selectivity of analytical reactions; consequently many time-consuming separation steps in an analytical procedure may be eliminated.

In the last few years, trace analysis of solids by the double-focusing, spark-source mass spectrograph has come into its own, and it is growing very rapidly. J. R. Woolston described this analytical technique which is characterized by very high sensitivity (1 to 10 atomic parts per billion) and one-shot complete coverage of essentially all elements in the periodic table. High sensitivity is obtained in the direct analysis of conductive, solid samples which serve as the spark electrodes. Insulators, powders, and surface films can also be analyzed with special electrode techniques, but with detection sensitivities limited usually to 0.1 to 1 part per million. With the current state of knowledge, the absolute accuracy of impurity determinations is limited to a factor of three or greater due to variations in ionization efficiency and the use of a photoplate detector. R. E. Honig discussed some recent developments. The focused beam from a ruby laser has been used to heat a microvolume of the sample to temperatures between 6000° and 10 000°K and produce thermal emission of large pulses of neutral atoms and molecules, electrons, and positive ions. The electrons can be used to ionize the neutrals, permitting analyses to be made to 10 parts per million. New ion sources have been developed based on

a pulsed low-voltage arc discharge triggered by a high-voltage pulse of microsecond duration. Compared with the conventional rf source, the ions produced by this source have a smaller energy distribution (less than 200 volts), so that the ion currents obtainable are substantially higher, the sample consumption is lower, and higher detection sensitivities are possible. In discussion, E. B. Owens (MIT Lincoln Laboratories) pointed out that the main weakness of mass spectrography, at present, is its poor accuracy as indicated by a comparison of results from different laboratories on the same samples.

In contrast with the techniques previously described for determining elemental composition, M. D. Coutts discussed the use of electron microscopy and electron diffraction for investigating habit and structure. New techniques have been developed for surface studies on semiconductors. In one, gold nuclei are deposited on silicon, germanium, or other surfaces by displacement or plating of ions in solution. These particles form preferentially on fine cleavage steps and on other surface defects which can be revealed by stripping the gold particles off via a deposited carbon film. Surface imperfections representing deviations that would otherwise be below the resolution limit of the microscope are revealed and, in addition, the gold particles take up the orientation of the substrate as revealed by electron diffraction. Figure 1 shows traces of three slip planes as revealed by gold nuclei deposited on a cleaved germanium crystal.

J. Kurshan described the operation of Industrial Reactor Laboratories, Inc., a nuclear reactor installation jointly owned by ten companies and operated for them by Columbia University. IRL comprises a five-megawatt swimming pool reactor and laboratory building in Plainsboro, N.J. Analytic uses of the reactor by RCA have included radioactive tracers, activation analysis, and neutron diffraction. Special radioactive isotopes have been prepared by neutron bombardment at IRL enabling the control of purity, packaging, dosage, and delivery time. At RCA, neutron activation analysis often gave way to more convenient mass spectrometry. Activation analysis, however, can be convenient and fast and provides greater absolute accuracy which becomes especially important in the range of impurity concentrations below one part per million. Both x-ray and neutron diffraction are used in the determination of crystal structure and both methods were described by J. G. White. Where either might be used, x-rays are to be preferred because of the cost of neutron-beam facili-

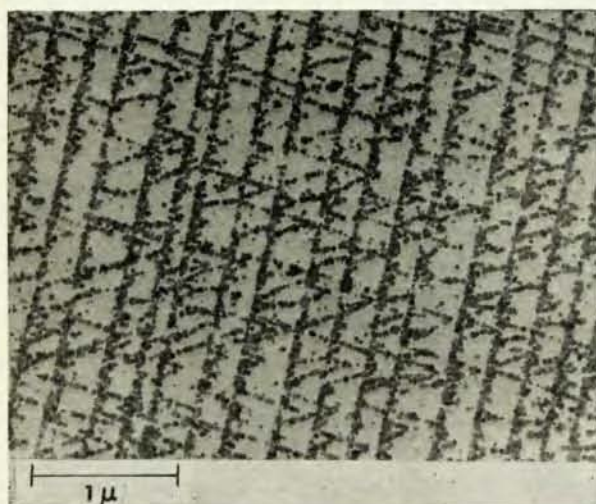


Fig. 1. Electron micrograph showing decoration of cleaved germanium crystal by electroplated gold nuclei

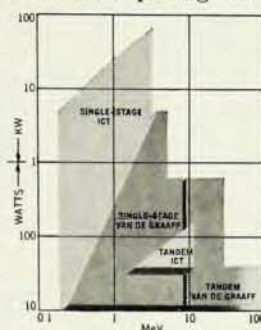
CHARGED PARTICLES



THE ICT CONCEPT: new high-current machines emerging from HVEC research

Development of higher energy Van de Graaff particle accelerators which retain high beam precision, stability, and homogeneity, remains a continuing contribution by HVEC to "energy-oriented" research.

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ICT 300	300	15 mA	4'4"	1.32	4	1.2
ICT 500	500	10 mA	5'3"	1.60	4	1.2

The second system utilizes a rigid transmission line to transmit electrical power to the accelerator terminal.

	ENERGY (MeV)	CURRENT	DIMENSIONS Length Feet	DIMENSIONS Length Meters
4 MeV ICT				
Positive Ions	1.5-4	3 mA	26'6"	8.08
Electron Conversion	1.5-3	10 mA	26'6"	8.08
3 MeV ICT				
Electrons	1.5-3	20 mA	29'	8.84

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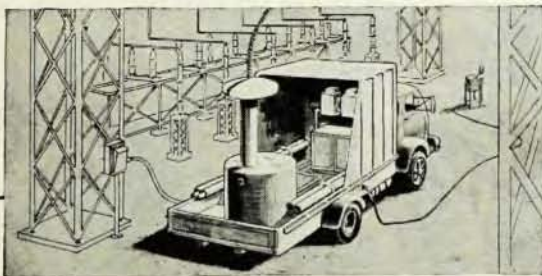
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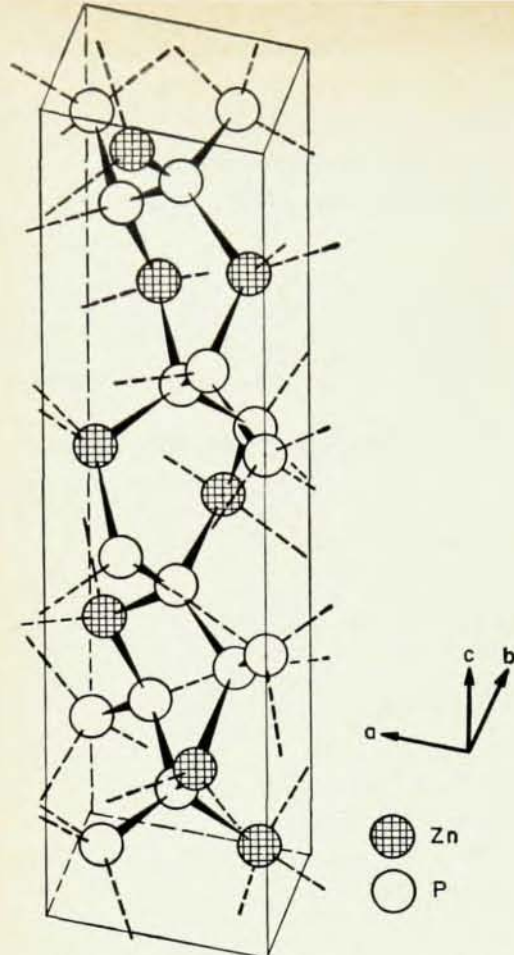


Fig. 2. Atomic arrangement of a one-unit cell of ZnP_2 . Dotted lines complete tetrahedral bonding to atoms outside the cell

ties. Figure 2 is a view of the atomic arrangement of one unit cell of red, tetragonal ZnP_2 as obtained from x-ray diffraction data. Neutron diffraction has two principal advantages as compared with x-ray diffraction: the positions of light atoms can be found in the presence of heavy atoms, and the arrangement of the magnetic spins can be deduced.

R. Black (US Naval Research Laboratory) pointed out that close cooperation is needed between the analytical chemist and the physicist in order to develop improved instrumental methods for analysis. In addition to such general facilities already mentioned above (Adler), NRL also has available a vacuum fusion analyzer for gases, an inert gas fusion analyzer, polarograph, atomic absorption flame spectrometer, electron probe analyzer (under development), and a 14-MeV neutron generator (on order). A noteworthy project involving broad-range trace analysis at NRL was the high-purity iron program. Analysis was required for 55 elements to an accuracy of one part per million in the concentration range of 0 to 5 parts per million. The project was completed successfully with four man-years of effort.

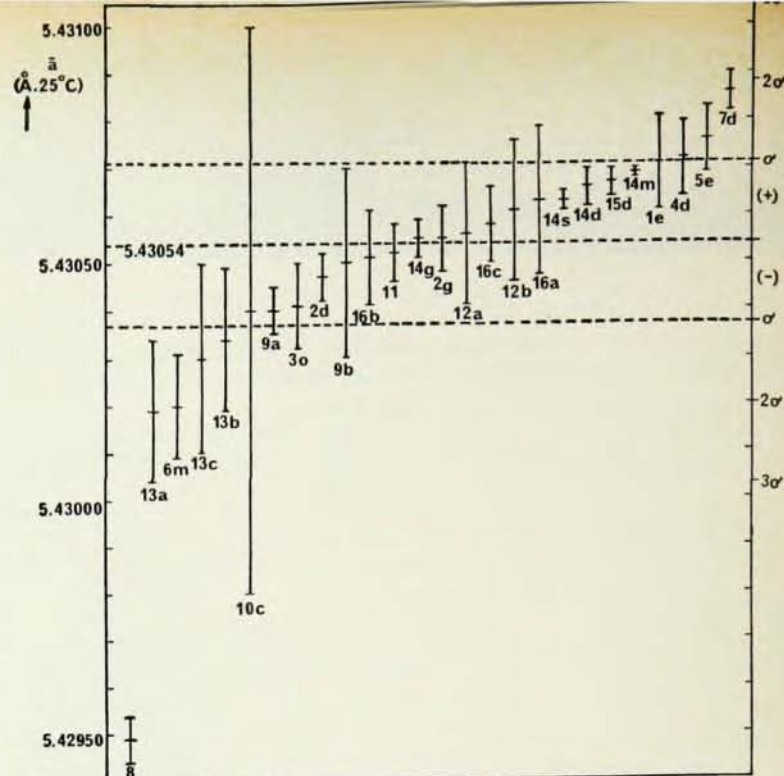


Fig. 3. Distribution of mean values of lattice parameter of silicon [Acta Crystallographica, Vol. 13, p. 843 (1960)]

Vacuum fusion is particularly applicable to the determination of oxygen, hydrogen, and nitrogen. As described by O. Gates (NRL), the basic technique is to melt the sample in a graphite crucible. The oxides are reduced by the graphite with the release of carbon monoxide; nitrides and hydrides are decomposed thermally. The gases are removed from the furnace area with a diffusion pump, collected, and analyzed. The sensitivity of the vacuum fusion method for determining hydrogen in steel has been extended to one-tenth part per million. A recent enhancement of the vacuum fusion method has come from Bell Telephone Laboratories: small thin-film samples on glass can be analyzed with a xenon discharge lamp producing surface temperatures as high as 8000°C . A sensitive gas chromatograph is used as the detector.

The potential use of nuclear magnetic resonance and electron paramagnetic resonance in analysis was discussed by H. C. Allen (National Bureau of Standards). Although NMR has already established itself with the organic chemist as a routine method of getting structural information, it does not appear promising as a tool for trace analysis. Present sensitivity is 4×10^{-3} mole for protons, and the sensitivity is much less in solids. Electron spin resonance has somewhat more potential although it is limited to paramagnetic systems; that is, some transition metals, some rare earths, and free radicals. In special systems, its sensitivity can be

extremely high, e.g., Mn^{++} has been observed with a detectability of at least 3×10^{12} spins or 5.5×10^{-11} grams. In solids, however, 0.01 percent impurity can just be detected at present.

In discussing high-resolution powder diffractometry, W. Parrish (Philips) rightly assumed that there was no longer a need to justify x-ray diffraction in a solid-state materials laboratory. Even so, he noted that we are still working in the parts-per-thousand range in precision lattice parameter determinations. Figure 3 is the result of a "round-robin" comparison of analyses conducted among acknowledged leaders in these measurements. The agreement among laboratories is only one part in 10 000, which is about an order of magnitude poorer than the precision often claimed in the literature. It appears that the random errors have been handled in individual laboratories better than the systematic errors. Thus, the distinction between precision and accuracy must be emphasized. It is in the field of systematic error reduction that further improvements have to be made in physical measurement techniques. At Philips, sophisticated techniques are being developed for accurate lattice parameter determination on an absolute basis by determining the centroid of the complete line profile. While this method has limitations, it provides a possibility of putting other techniques involving peak measurement of line profiles on a correct empirical basis. Concerning phase identification, in the past 25 years an order-of-magnitude improvement has been made in sensitivity and resolution of powder patterns, but another order of magnitude improvement is being sought. If resolution is sacrificed for speed, aberrations resulting from the slit system can broaden the line and decrease the peak-to-background ratio. Just as important as increasing resolution is increasing dispersion, which can be done by using longer wavelengths. It has been difficult to use chromium radiation, but improved techniques have been developed that will increase the intensity obtained by a factor of fifteen.

Under certain conditions, nearly perfect crystals as thick as a millimeter will transmit x-rays with very little absorption. S. O'Hara (Westinghouse) discussed this anomalous x-ray transmission and its application to the study of imperfections in crystals. Defective regions of the crystal such as precipitates or dislocations will absorb the x rays and show up on a photographic plate, their outline being sharpest when they are near the exit surface of the crystal. The limit of detection of defects is about 0.3 millimeters from the exit surface and disturbed regions of 50μ or greater can

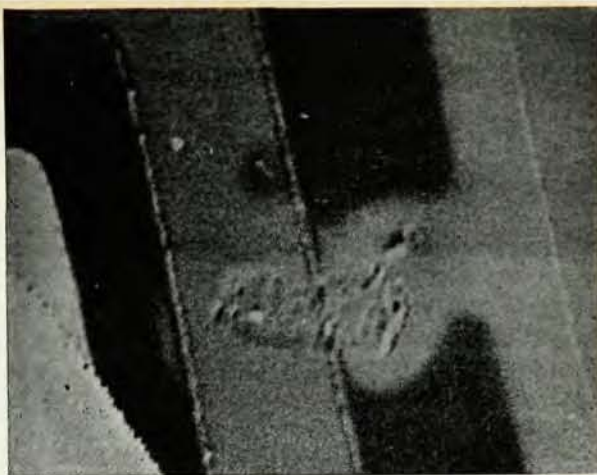


Fig. 4. Inhomogeneity in diffusion pattern revealed by scanning electron microscope [Everhart, Wells, and Mata, *Journal of the Electrochemical Society* (1964)]

be made visible. Anomalous transmission can be observed for a dislocation density less than about $10^6/\text{cm}^2$. All that is needed is a line-focus source of x-rays and means for orienting the surface of the crystal to within about 5° . A principal advantage of the technique lies in its simplicity.

Emphasis on applications to analyzing electronic devices was chosen by O. C. Wells (Westinghouse) in discussing the scanning electron microscope. In this instrument an electron beam scans the specimen, and secondary electrons are collected from its surface. This gives a signal which is used to modulate the brightness of a cathode-ray tube scanned synchronously with the electron beam. Figure 4 shows a typical picture obtained with the instrument when scanning a solid-state, integrated circuit. The application of biases to the electrodes can increase the contrast, since the voltage at the specimen affects the trajectories of the secondary electrons, and the aperture selects only a limited distribution of these. Devices can also be fabricated with the help of the instrument. As an example, the electron beam has been used to polymerize a photo resist coating to produce a pattern of lines 1 micron wide. At the same time the electron beam can be used to extract information from the work piece. This concept of incorporating analytical techniques into the fabrication process is an important approach to improving processing quality.

Electron probe microanalysis was discussed by R. Roy (Pennsylvania State University) with particular emphasis on its adaptability to new situations, e.g., the examination of powders and thin films. There is already a wealth of experience and a good literature on application to metals. The basic probe provides for scanning a specimen with an electron beam and detecting either the

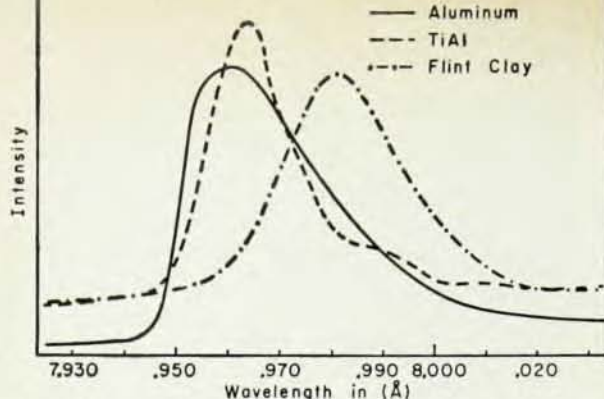


Fig. 5. Effects of structure on aluminum emission band as observed with the electron probe

back-scattered electrons or the x rays generated. A light pipe has been used to add a photoluminescent channel which gives the probe the potential of getting down into the parts-per-million sensitivity range. The sensitivity and speed of the probe for elemental analysis compares favorably with wet chemical analysis. However, the electron probe should be reserved for cases where there is segregation on a microscale, rather than for general trace analysis. Valence states and the immediate nearest neighbor coordination of an ion have been investigated by looking at the *K*-emission wavelength, thus going beyond mere elemental analysis. Figure 5 shows how metallic aluminum can be distinguished from aluminum in a titanium-aluminum alloy and from aluminum surrounded by six oxygen atoms. There is also a significant difference between four- and six-coordinated aluminum.

Neutron activation analysis is a well-established method especially useful for the accurate determination of trace impurities. In discussing this technique, W. W. Meinke (NBS) emphasized that it is all the more powerful because of recent developments in neutron sources and in sample treatment. Those who are not actively using this method were urged to take a fresh look at its potential. Commercial services are available now and, in addition, some 75 laboratories have their own neutron generators which permit activation analysis with useful, though not high, sensitivities. A neutron generator does provide speed in analysis and one large analytical laboratory is doing 40 percent of its elemental analysis by neutron activation, and most of the rest by x-ray fluorescence. In neutron activation analysis a precision of 5 percent is readily achieved at the nanogram level for many elements. A number of elements are less readily detectable by activation analysis. These are H, He, Be, B, C, N, O, F, Ne. In doing gamma-ray spectrometry, the Compton-scattering background adds up for different impurities and it is not

feasible to separate the data for more than six or eight superimposed energy distributions. Beyond that, chemical separation is needed to eliminate other interfering elements even if the yield of the element of interest is less than 100 percent. We can even expect automation of the chemistry in the near future.

Measurements of residual resistivity (at liquid-helium temperature) provides a rapid and highly sensitive determination of the impurity content of metals. At these temperatures, the resistivity is controlled largely by scattering with lattice defects and impurities. Although a measurement precision of a few percent is easily achieved, unfortunately the measurements provide almost no information as to which specific impurities are present, and the scattering cross-section for different impurities can vary widely. A. A. Johnson (Materials Research Corporation) discussed the application of residual resistivity measurements, using the four-point probe method, to the body-centered cubic transition metals. Point defects and impurities produce about the same effect on the resistivity, while the effects of grain boundaries and dislocations can usually be neglected. In these metals, impurities in the part-per-million range are easily detected. This method is especially useful in determining relative impurity concentrations in a given material during a purification process. For example, the purity of a metal following solid-state electrolysis has been monitored by this technique. C. H. Rosner (GE) has also used residual resistivity to measure the total impurity content in pure metals by employing a contactless technique. The contactless method depends on the characteristic decay of magnetically induced eddy currents. If a steady-state magnetic field is applied to the sample and then suddenly removed, the voltage generated in a pickup coil is directly related to the resistivity and approaches a simple exponential decay with a characteristic time constant. Spatial resolution to a few millimeters along the length of a bar is possible, so that the general impurity content along a zone-refined ingot is easily determined. Residual resistivity and direct analysis supplement each other; the resistivity measurements give an indication as to whether the analysis has adequately accounted for the impurities present. There is a lower limit to specimen size because of scattering at the surface of high-purity materials with long mean free paths.

It is expected that this symposium will be followed by others, also under ARPA sponsorship, on important materials research topics (e.g., crystal growth and research on structural-type materials).