

SOLID STATE PHYSICS LITERATURE GUIDES
Volume 3

GROUPS IV, V, AND VI
TRANSITION METALS
AND COMPOUNDS
Preparation and Properties

Solid State Physics Literature Guides

Prepared under the auspices of the Research Materials Information Center,
Oak Ridge National Laboratory

General Editor: T. F. Connolly

*Solid State Division
Oak Ridge National Laboratory*
Oak Ridge, Tennessee*

- Volume 1: Ferroelectric Materials and Ferroelectricity—1970
- Volume 2: Semiconductors—Preparation, Crystal Growth, and Selected Properties—1972
- Volume 3: Groups IV, V, and VI Transition Metals and Compounds—Preparation and Properties—1972
- Volume 4: Electrical Properties of Solids—Surface Preparation and Methods of Measurement—1972

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TRANSITION METALS
AND COMPOUNDS**
Preparation and Properties

**Edited by
T. F. Connolly**

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Introduction

The material in this collection is based mainly on papers actually received by the Research Materials Information Center, although some references are included on specific recommendations. While this might exclude a few relevant papers, it also excludes a much larger number of nonpertinent references that might be chosen on the basis of deceptive titles or inadequate abstracts.

For any collection of this sort the question of what should or should not be included often involves individual bias or differences of opinion of the meaning of terms, and the criticisms of two experts in the same field are often contradictory. For this reason most compilations in this series, in addition to organization under appropriate subject headings, contain one or more sections entitled "Reviews, Bibliographies, and Compilations," in which references to peripheral related subjects are deliberately included. In all other sections the effort is to be as specific as possible, with borderline references kept to a minimum.

At this writing, there are over 70,000 searchable references in the RMIC collection on solid-state inorganic materials science, and the coverage of the field is good back to 1960, although many earlier references are included. Still, there will be omissions and errors in compilations drawn from the collection, and any pointed out to us will be corrected in future editions. (Such corrections should be sent to the Center and not to the publisher.)

The timeliness of these compilations, as well as our ability to answer daily inquiries, depends very largely on the continued receipt by the Center of all papers, reprints, reports, and preprints within our scope. These should be mailed to

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Preface

Since 1963 the Research Materials Information Center has been answering inquiries on the availability, preparation, and properties of ultrapure inorganic research specimens. It has been possible to do this with reasonable efficiency by searching an automated, coded microfilm collection of the report and open literature and of data sheets and questionnaires provided by commercial and research producers of pure materials.

With the growth of the collection to over 70,000 documents and the increase in the demand for more general background information, it has been necessary to compile bibliographies on an increasing variety of subjects. These have been used as indexes to the microfilmed documents for more efficient searching, and in the past distributed in response to individual requests. However, their size and number no longer permit so casual and uneconomic a method of distribution. The "ORNL Solid State Physics Literature Guides" is a practical alternative.

Scope of This Bibliography

The scope of the bibliography is that of the Research Materials Information Center: emphasis is on materials preparation, ultrapurification, crystal growth, characterization, and basic physical properties of research specimens. Engineering and mechanical properties are not included except incidentally in references to handbooks and some serial compilations. The one exception to the coverage indicated by the title is the inclusion of Groups VII and VIII in the section on chalcogenides. The differences between numbers of subdivisions and numbers of references among the major divisions of the bibliography also reflect the coverage of the Center: the greater part of the collection is devoted to the single elements and the oxides.

Organization

The subject organization of the bibliography is given by the Table of Contents, which represents the structures of six separate bibliographies compiled by the RMIC. Sections entitled "General" include listings of reviews, bibliographies, and compilations, or collections of a variety of elements or compounds not subsumable under other headings. Under each subheading the arrangement is chronological, with 1971 first, and alphabetical by first author within each year.

To the rear of this Preface, is an indexed list of other information sources and of new journals or serial publications in the field of solid-state materials.

Acknowledgment

I am grateful to R. E. Reed, of the ORNL Solid State Division, for his detailed review of the sections on the single elements and the oxides and for useful suggestions on their reorganization. (Errors and omissions, however, are my own

responsibility.) To Betty Edwards and Emily Copenhaver my thanks for what must have seemed endless typing, retyping and correcting of these bibliographies over a span of years.

Availability of Documents

U. S. Government contractor reports, usually identified by an alpha-numeric report number, can be purchased from

National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151

and, often, on request from the issuing installation.

USAEC reports are also available from

International Atomic Energy Agency
Kaerntnerring A 1010
Vienna, Austria

National Lending Library
Boston Spa
England

Monographs and reports of the National Bureau of Standards are for sale by

Superintendent of Documents
U. S. Government Printing Office
Washington, D. C. 20402

Theses, listed as Dissertation Abstracts + number, are available in North or South America from

University Microfilms
Dissertation Copies
P. O. Box 1764
Ann Arbor, Michigan 48106

and elsewhere from

University Microfilms, Ltd.
St. John's Road
Tylers Green
Penn, Buckinghamshire
England

Other Information Centers and New Journals

Field	Information centers and other sources	New journals and serials
Ultrapurification and crystal growth	4, 8, 11, 13, 15, 16, 19, 20, 21, 28, 30, 32, 33, 42, 58, 59	9, 11, 15, 24, 31, 32

Field	Information centers and other sources	New journals and serials
Characterization		
Miscellaneous	3, 4, 8, 11, 13, 16, 19, 20, 21, 26, 28, 30, 31, 32, 33, 35, 37, 38, 39, 40, 42, 46, 53, 56, 58, 60, 61, 62	1, 3, 4, 8, 11, 15, 17, 24, 25, 28, 29, 30, 31, 32
Activation analysis	1, 2, 6, 38, 43, 48, 57	12, 22
Neutron diffraction	12, see also Miscellaneous and Activation Analysis	
Mass spectrometry	17, 18, 38, 44, 45	6, 14, 21
Optical methods	5, 27, 39, 54	2, 17, 18, 19, 20, 27, 30
Electron diffraction and microscopy	9, 10, 27, 41, 50	16, 17, 30
X-ray diffraction and spectroscopy	5, 9, 10, 12, 22, 27, 34, 39, 40, 41, 50, 51, 52	17, 30
Electron microprobe analysis	See Electron Diffraction and Microscopy; X-Ray Diffraction and Spectroscopy	16
Measurement of electrical properties	13, 14, 20, 29, 33, 49	25
Thermal methods	4, 7, 23, 24, 25, 30	5, 13, 23
Resonance methods	3, 39, 47, 55	10
Mossbauer effect	3	
Field or ion emission		6

Specialized Information Centers and Other Sources

1. Activation Analysis Documentation Center, Akademiai Kiado, Publishing House of the Hungarian Academy of Sciences, Publicity Department, P.O. Box 24, Budapest 502, Hungary. (5500 punched cards, searchable by elements, classes of materials, discipline, instrumentation; 1935-1968; in English).
2. Activation Analysis Research Laboratory, Texas Agricultural and Mechanical University, College Station, Texas, 77843.
3. Alloy Data Center, Alloy Physics Section, Metallurgy Division, National Bureau of Standards, Washington, D. C. 20234, telephone 301-921-2917. Critically evaluated data on physical properties of metals and alloys.
4. American Society for Metals – Documentation Service, Metals Park, Ohio 44072, telephone 216-ED 8-5151. Includes electronics solid state physics, inorganic chemistry; computer searches; publishes ASM Review of Metal Literature.
5. Atomic Energy Levels Data and Information Center, Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234, telephone 301-921-2014. Provides critical appraisal of data on atomic spectra; classification of spectral lines and determination of atomic energy levels; coordination of experimental work in the laboratories working in this field.

6. Zentralstelle fuer Atomkernenergie—Dokumentation, Frankfurt am Main, West Germany. Compiles bibliographies in nuclear science and technology, including several extensive and detailed compilations on activation analyses.
7. Chemical Thermodynamic Data Center, Physical Chemistry Division, Institute for Basic Standards, National Bureau of Standards, Gaithersburg, Maryland, telephone 301-921-2467. Thermochemical data, heats of formation, free energy of formation of chemical substances.
8. Cobalt Information Center, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio 43201, telephone 614-299-3151, extension 2234. (Main office: Centre d'Information du Cobalt, S. A., 35 rue des Colonies, Brussels 1, Belgium; Branch offices: Cobalt Information Centre, 7 Rolls Building, London E. C. 4, England; and Kobalt-Information, Elisabethstrasse 14, Dusseldorf, Germany). Publishes the journal Cobalt; bibliographies; answers specific inquiries and provides technical assistance on cobalt (and alloys and compounds).
9. Commission on Crystallographic Data, International Union of Crystallography. Chairman: Dr. F. W. Matthews, Central Technical Information Unit, Imperial Chemical Industries Ltd., Imperial House, Millbank, London S. W. 1, United Kingdom.
10. Crystal Data Center, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, telephone 301-921-2837. Crystallographic data on all solids; data and related information on unit cell dimension of crystal materials. Purpose is to revise and bring up to date the volume of Crystal Data; to maintain this semicritical compilation; to identify crystalline materials by single crystals; and to collect and maintain data and information on crystalline materials.
11. Centre de Documentation sur les Synthèses Cristallines, Laboratoire de Physique Moléculaire et Cristalline, Faculté des Sciences, Place Eugene-Bataillon 34-Montpellier, France. Identifies European crystal growers by country installation, and material. Up-dated loose-leaf sheets.
12. International Data Center for Work on Crystallography, University Chemical Laboratory, Cambridge, England. Works closely with all groups involved in crystallographic documentation and data evaluation. At present only carbon-containing structures are compiled for data obtained by x-ray and neutron diffraction (for a computer oriented file).
13. Electronic Materials Information Center, Royal Radar Establishment, St. Andrews Road, Gt. Malvern, Worcestershire, England.
14. Electronic Properties Information Center, Hughes Aircraft Company, Centinela and Teale Streets, Culver City, California 90230, telephone 213-391-0711, extension 6596.
15. Bureau d'Information sur les Matériaux ultra Purs, IMP - Inspection Générale, C.E.A. 29, rue de la Fédération, B. P. 510, Paris (XV), France, telephone 273 60-00 poste 55-95. Inquiry service on purification and availability of ultrapure metals.
16. Isotopes Information Center, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37830, telephone 615-483-8611, extension 3-1742; Federal Telecommunication System No. 615-483-1742. Information primarily on production and uses of radioisotopes in industry and research. Includes unusual counting methods or new instrumentation for detection of isotopes, instruments that use isotopes in their operation.
17. Mass Spectrometry Data Center, National Bureau of Standards, Washington, D. C. 20234, telephone 301-921-2173.
18. Mass Spectrometry Data Center, Building A 8.1, Atomic Weapons Research Establishment, Aldermaston, Berks., England. (MSDC Mass Spectra Data Sheets)
19. Rare-Earth Information Center, Institute for Atomic Research, Iowa State University, Ames, Iowa 50010, telephone 515-294-2272. Analytical, inorganic, and physical chemistry of the rare-earth elements and compounds; solid state physics and metallurgy. Publishes reviews, compilations, and bibliographies. Inquiry service by mail and telephone.
20. Research Materials Information Center, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830,

- telephone 615-483-8611, extension 3-1287; Federal Telecommunication System No. 615-483-1287. Provides references on availability, purification, crystal growth, and properties of all ultrapure inorganic research specimens.
21. The Selenium—Tellurium Information Service, Selenium—Tellurium Development Association, Inc., 345 East 47th Street, New York, New York 10017, telephone 212-688-2632. Publishes periodic selenium and tellurium bibliography; inquiry service.
 22. SHARE Library System, a compilation of x-ray diffraction computer programs available on request. IBM Corporation, White Plains, New York.
 23. Thermodynamic Properties of Metals and Alloys, Lawrence Radiation Laboratory, University of California, Berkeley, California 94720, telephone 415-843-2740, extension 3817.
 24. Thermodynamics Research Center, Research Center of Texas A. and M. University, College Station, Texas 77843. Thermodynamic and other physicochemical properties; infrared, ultraviolet, Raman, mass, and nuclear magnetic resonance spectral data.
 25. Thermophysical Properties Research Center, Purdue University, 2595 Yeager Road, West Lafayette, Indiana 47906, telephone 317-743-3827. Provides reference data based on integrated programs of critical evaluation.
 26. Analytical Abstracts. Society for Analytical Chemistry, 9-10 Savile Row, London, England.
 27. Bulletin Signalétique. Centre de Documentation du C.N.R.S., 15, quai Anatole-France, 75-Paris-VIIe, France. Section 160 - Structure de la matière, I. Physique de l'état condensé. Physique atomique et moléculaire. Spectroscopie; Section 161 - Structure de la matière, II. Cristallographie; Section 170 - Chimie. Chimie générale et chimie physique. Chimie minérale. Chimie analytique. Chimie organique. Section 761 - Microscopie Electronique. Diffraction Electronique. (All four are monthly abstract publications covering world literature; indexed by subject, author, and installation.)
 28. Chemical Abstracts now markets a magnetic tape service. Inquiries should be addressed to Chemical Abstracts, Division of American Chemical Society, Ohio State University, Columbus, Ohio 43210, telephone 614-293-5022.
 29. Electrical and Electronics Abstracts; also Current Papers in Electrical and Electronics Engineering. Institute of Electrical and Electronics Engineers, 345 East 47th Street, New York, New York 10012.
 30. Metals Abstracts. American Society for Metals, Metals Park, Ohio 44073 or The Institute of Metals, 17 Belgrave Square, London S.W. 1, England. Index terms and complete literature citations available on magnetic tapes for 1968-69. Also 1965-67 for Review of Metal Literature.
 31. Nuclear Science Abstracts. Bimonthly; abstracts of world literature, indexed by material, subject, author, and installation. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
 32. Physics Abstracts. American Institute of Physics, Office of Publications, 335 East 45th Street, New York, New York 10017.
 33. Solid State Abstracts. Abstracts on preparation and properties of high-purity inorganic compounds. Cambridge Communications Corporation, 238 Main Street, Cambridge, Massachusetts 02142.
 34. X-Ray Fluorescence Spectrometry Abstracts, Science and Technology Agency, 3 Dyers Building, London E. C. 1, England. New quarterly publication; surveys international literature including conference proceedings and unpublished reports on theory and applications.
 35. Periodic bibliographic surveys on most techniques appear in Analytical Chemistry. American Chemical Society, 1155 Sixteenth Street, N. W., Washington, D.C. 20036.
 36. Journal of Chemical Documentation. American Chemical Society, 1155 Sixteenth Street, N. W., Washington, D.C. 20036.
 37. Current Contents. Institute for Scientific Information, Inc., 325 Chestnut Street, Philadelphia, Pennsylvania 19106. Prints tables of contents of current journals in chemistry, physics, and other fields.

38. Commission for the Establishment of Analytical Methods. Commission d'Établissement des Méthodes d'Analyse (C.E.T.A.M.A.), Commissariat à l'Énergie Atomique, 75-Paris, France. Gamma and mass spectrometry, statistical methods, tabulation of radioactive half-lives; reviews.
39. CODATA International Compendium of Numerical Data Projects, Springer Verlag, New York; Heidelberg; Berlin (1969). Identifies, with address, international centers, data projects, and publications concerning (a) optical, x-ray, mass, and magnetic resonance spectra; (b) crystallographic, electrical, and magnetic properties; (c) thermophysical properties; (d) nuclear and isotopic data. Published form and availability of data are noted in each case.
40. Crystal Structures, 2nd edition, R. W. G. Wyckoff (Wiley-Interscience, New York; London; Sydney), Vol. 1; 1963, 467p.; Vol. 2; 1964, 588p.; Vol. 3; 1965 981p.; Vol. 4; 1968, 566p.; Vol. 5, 1966, 785p.
41. A Crystallographic Book List, Commission on Crystallographic Teaching, International Union of Crystallography (1965). (About 800 books on crystallography and related subjects; classification by subjects; many cross references)
42. Pierre de la Breteque, Directeur de Recherches, Société Française pour l'Industrie de l'Aluminium, 134 Chemin des Aygaldes, 13 Marseille 15e, France. Publishes annual bibliographies on gallium and compounds (including III-V, III-VI, and ternaries) covering preparation and physical properties, containing phase diagrams of new compounds.
43. Gamma-Ray Spectrum Catalogue, National Reactor Testing Station, P.O. Box 1845, Idaho Falls, Idaho 83401, director: R. L. Heath, telephone 208-522-4400, extension 4447. (Gamma-ray reference spectral)
44. Catalog of Mass Spectral Data (loose-leaf data sheets and supplements), Thermodynamics Research Center, Texas A. and M. Research Foundation, F. E. Box 130, College Station, Texas 77843.
45. Index to Mass Spectral Data, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. Available as ASTM-AMD 10 A-C and 11A (1969), punched cards.
46. For a complete list of Standard Reference Materials available from the National Bureau of Standards, see Catalog of Standard Reference Materials, NBS Spec. Publ. 260 (July 1970 ed.) for sale by the superintendent of Documents, U. S. Government Printing Office, Washington, D. C. for 75 cents. A Standard Reference Material Availability and Price List is issued semiannually and supplied to users on request.
47. NMR, NQR, EPR Current Literature Service issued by the publishers of DMS - Documentation of Molecular Spectroscopy in association with the Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund and DMS Scientific Advisory Board, London (Butterworth and Company, Publishers, Ltd., London). (Resonance literature from 1963; reference list and card index; 600 journals covered).
48. Index de la Littérature Nucléaire Française. Monthly computer printout of abstracts; titles in French and English; includes general and analytical chemistry, activation analysis, neutron diffraction, accelerators, neutron sources. Key-word-in-context indexes in French and English; author and installation indexes. (Service Central de Documentation du Commissariat à l'Énergie Atomique, Centre d'Études Nucléaires de Saclay, B. P. No. 2, 91-Gif-sur-Yvette, France).
49. A Joint Program on Methods of Measurement for Semiconductor Materials, Process Control and Devices has been undertaken (in 1968) by the National Bureau of Standards, Electronic Technology Division, Washington, D. C. [J. C. French is coordinator of the program; NBS-TN-472 (Dec. 1968), MBS-TN-475 (Feb. 1969), NBS-TN-488 (July 1969), NBS-TN-495 (Sept. 1969), and NBS-TN-520 (March 1970) are recent reports.]
50. Powder Diffraction Data File - X-Ray or Electron. Approximately 10,000 patterns, issued in the form of 3 x 5 cards; five types of indexes are available. American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19104, telephone 215-563-5315. But see Computer detected errors in the ASTM x-ray powder diffraction file, M. C. Nichols (Sandia Corp., Livermore, California), SCL-DR-70-48 (April 1970), 26p.
51. Structure Reports, Vol. 22 (1958-1968), 890p.; Vol. 24 (1960-1968), 795p.; Vol. 25, Cumulative Index for Vols.

- 15-24 (1969), International Union of Crystallography, Commission on Structure Reports (Oosthoek, Utrecht, Netherlands). (Principally by x-ray but includes results of electron and neutron diffraction and other methods)
52. *Advances in X-Ray Analysis*. Proceedings of Annual Conference on Applications of X-Ray Analysis, University of Denver (Plenum Press, New York).
 53. World Meetings Information Center, CCM Information Corp., 909 Third Avenue, New York, New York 10022. Publishes Current Index to Conference Papers in Chemistry. (Vol. 1, No. 11 in July 1970).
 54. Atomic Absorption and Flame Emission Spectroscopy Abstracts. Science and Technology Agency, 3 Dyers Building, London, E. C. 1, England.
 55. Nuclear Magnetic Resonance Spectrometry Abstracts. Science and Technology Agency, 3 Dyers Building, London, E. C. 1, England. (First issue January 1971)
 56. Diffusion in Metals and Alloys Data Center, Metal Physics Section, Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234. Diffusion coefficients and activation energies.
 57. Activation Analysis Information Center, Analytical Chemistry Division, National Bureau of Standards, Washington, D. C. 20234.
 58. Ferroelectric Materials and Ferroelectricity, T. F. Connolly and Errett Turner, eds., Vol. 1 of ORNL Solid State Physics Literature Guides (IFI/Plenum, New York, Washington, London, 1970), 685p.
 59. Semiconductors: Preparation, Crystal Growth, and Selected Properties, T. F. Connolly, ed., Vol. 2 of ORNL Solid State Physics Literature Guides (IFI/Plenum, New York, Washington, London, 1971). (Material-organized bibliography of Research Materials Information Center references received thru 1970)
 60. Computer-Based Chemical Information Services, Edward M. Arnett, *Science* 170, 1370-76 (1970). (Review of some services available)
 61. Annotated Accession List of Data Compilations of the Office of Standard Reference Data, Herman M. Weisman and G. B. Sherwood, NBS Tech. Note 554 (1970). (About 1300 reference data compilations, critical reviews, bibliographies, and other ancillary reference works)
 62. Diffusion Information Center, 22447 Lake Road, Cleveland, Ohio 44116, or P. O. Box 505, CH-4500 Solothurn, Switzerland.

New Journals and Serials

1. *Analytical Letters*. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 10016. (Vol. 1 in 1967)
2. *Applied Spectroscopy Review*. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 10016. (Vol. 1 in 1967)
3. *Chemical Instrumentation*. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 10016. (Vol. 2 in 1969)
4. *CRC Critical Reviews in Analytical Chemistry*. Chemical Rubber Co., 18901 Cranwood Parkway, Cleveland, Ohio 44128. (Vol. 1 in 1971)
5. *High Temperature Science*. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 10003. (Vol. 1 in 1969)
6. *International Journal of Mass Spectrometry and Ion Physics*. Elsevier Publishing Co., P. O. Box 211, Jan Van Galenstraat 335, Amsterdam, Netherlands. (Vol. 2 in 1969)
7. *Journal of Chemical Thermodynamics*. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003 or 17 Old Queen St., London S. W. 1, England. (Vol. 1 in 1969)
8. *Journal of Chromatographic Services*. Preston Technical Abstracts, 909 Pitner, Evanston, Ill. 60602.
9. *Journal of Crystal Growth*. North Holland Publishing Co., P. O. Box 103, Amsterdam, Netherlands. (Vol. 1 in 1967)

10. Journal of Magnetic Resonance. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. (Vol. 1 in 1969)
11. Journal of Materials Science. Chapman and Hall, 11 New Fetter Lane, London E. C. 4, England. (Vol. 1 in 1966)
12. Journal of Radioanalytical Chemistry. Elsevier Publishing Co., Box 211, Amsterdam, Netherlands. (Vol. 1 in 1968)
13. Journal of Thermal Analysis. Heyden and Son, Ltd., Spectrum House, Alderton Crescent, London N. W. 4, England. (Vol. 1 in 1969)
14. Mass Spectrometry Bulletin, Mass Spectrometry Data Centre. Her Majesty's Stationary Office, P. O. Box 569, London, S. E. 1, England.
15. Materials Research Bulletin. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N. Y. 10523. (Vol. 1 in 1966)
16. Micron, The International Quarterly, Journal of Electron Microscopy, Electron Probe Micro-Analysis and Associated Techniques. Structural Publishers, Ltd., Watford, England. (Vol. 1, No. 1, June 1969)
17. Microstructures. A. Z. Publishing Corp., 647 North Sepulveda Blvd., Bel Air, Los Angeles, Calif. (Vol. 1, No. 1, August-September 1970)
18. Nouvelle Revue d'Optique Appliquee. Masson et Cie., 120 Bd. Saint Germain, Paris 6, France. (Vol. 1, No. 1, January-February 1970)
19. Optical Spectra. Optical Publishing Co., Inc., 7 North Pitt St., Pittsfield, Me. 01201. (Vol. 3 in 1969)
20. Optics Communications. North-Holland Publishing Co., P.O. Box 3489, Amsterdam, Netherlands. (Vol. 1 in 1969)
21. Organic Mass Spectrometry. Heyden and Sons Ltd., Spectrum House, Alderton Crescent, London N. W. 4, England.
22. Radiochemical and Radioanalytical Letters. Elsevier Publishing Co., Laussane, Switzerland. (Vol. 1 in 1969)
23. Thermochemica Acta. Elsevier Publishing Co., P. O. Box 211, Amsterdam, Netherlands. (Vol. 1, No. 1, March 1970)
24. Journal of Solid State Chemistry. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 10003. (Vol. 1 in 1970)
25. Journal of Non-Crystalline Solids. North-Holland Publishing Co., P. O. Box 3489, Amsterdam, Netherlands. (Vol. 4 in 1970)
26. Journal of Low Temperature Physics. Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 10011. (Vol. 2 in 1970)
27. Methodes Physiques d'Analyse. Services du GAMS, L.N.E., 1, rue Gaston-Boissier, Paris XV, France. (Review published quarterly by the Group for Advancement of Spectrographic Methods; Vol. 1 in March 1968)
28. International Journal of Nondestructive Testing. Gordon and Breach Science Publishers, 8 Bloomsbury Way, London W.C. 1, England. (Vol. 1 in 1970)
29. Diffusion Data. Diffusion Information Center, 22447 Lake Road, Cleveland, Ohio 44116. (Vol. 4 in 1970)
30. Crystal Lattice Defects. Gordon and Breach Science Publishers, 8 Bloomsbury Way, London W. C. 1, England. (Vol. 1 in 1970)
31. CRC Critical Reviews in Solid State Physics. Chemical Rubber Co., 18901 Cranwood Parkway, Cleveland, Ohio 44128. (Vol. 1 in 1971)
32. Comments on Solid State Physics (A Journal of Critical Discussion of the Current Literature). Gordon and Breach, Science Publishers, Inc., 150 Fifth Ave., New York, N. Y. 10011 or Gordon and Breach, Science Publishers, Ltd., 8 Bloomsbury Way, London W. C. 1, England.

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Foreword

Any specialized bibliography is at best a poor substitute for the detailed critical review, but in rapidly growing fields it is usually all that is available. In an attempt at a compromise between a simple listing of papers and the desirable exhaustive study, selected sections of the Solid State Physics Literature Guides will be introduced by fairly brief commentaries by experts in the various fields. In most cases the comments should be understood as necessarily tentative, with the authors working against a deadline not usual in more leisurely publications (for example, proof copies of the bibliographies had to be available to them before they could begin). Further, in view of the interim nature of the Guides, the authors of the comments have been asked to feel more free to conjecture than is usual in more formal papers.

We are all in their debt for their willingness to assume such a task under such conditions.

T. F. Connolly

PREPARATION METHODS FOR GROUPS IV, V, AND VI TRANSITION METALS

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Work on preparation methods of the Groups IV, V, and VI transition metals can be classified under four categories: (1) reduction, (2) refining or purification, (3) growth of single crystals, and (4) preparation of thin films. In the ensuing paragraphs an attempt is made to highlight the significant approaches and advances in each of these areas.

Reduction

The extractive metallurgy of all of the metals of these groups has undergone considerable change during the past two decades, as is evidenced by this compilation. Three general preparation methods — aluminothermic, carbothermic, and electrolytic reduction processes — dominate the current literature.

Processes based on the aluminothermic reduction of an oxide have been developed for niobium, tantalum, vanadium, chromium, and molybdenum. While this is a relatively old method dating back to the work of Goldschmidt at the beginning of this century, modern developments in high-temperature and high-vacuum technology have now made it commercially feasible. With the development of the electron-beam furnace, especially, the removal of any retained aluminum and oxygen as well as other residual volatile impurities from the base metal during melting has been greatly facilitated.

Carbothermic reduction processes have been reported for almost all of the metals included in this survey. The ores of the group IV elements are converted to the carbide in a carbon arc furnace, and then chlorinated for use in subsequent and/or reduction steps. The group V elements are prepared by reacting stoichiometric amounts of oxide and carbide *in vacuo* at elevated temperatures to obtain a metallic product usually containing undesirable amounts of carbon or oxygen. Refining of the product is generally required, although by careful control of the reaction conditions a high-quality product may be obtained directly as with niobium and tantalum.

Some effective work has been done on the electrowinning of most of these metals from a fused salt. The salt bath usually consists of a mixture of low-melting alkali halides in which the halide of the metal of interest is dissolved. While all of the transition metals are still produced primarily by metallothermic, carbothermic, or hydrogen reduction processes, electrowinning appears to offer an increasingly attractive alternative. Commercially feasible methods for pro-

* Work performed in the Ames Laboratory, U. S. Atomic Energy Commission.

ducing titanium and tantalum by direct electrolysis are known, and methods whereby all of the other metals included in this survey can be electrowon are described in the current literature.

The reduction processes discussed above yield products in solid ingot, sponge, coarse crystal, or powder form. The importance of fine powders in many electronic applications, especially tantalum, molybdenum, and tungsten, is evidenced by the amount of work devoted to this subject.

Refining

A plethora of refining techniques has been employed for these metals including vacuum extraction, zone refining, iodide decomposition, electrorefining, electrotransport, and sublimation.

Vacuum extraction involves the removal of volatile impurities by heating the metal under a low pressure. Most of these metals have relatively low vapor pressures at their melting points and hence can be purified with respect to oxygen and hydrogen as well as those metallic impurities having vapor pressures that are at least a factor of ten higher than that of the base metal. Electron-beam and vacuum-arc melting are widely used in the commercial purification of all of these metals except chromium. Some of the more volatile impurities such as hydrogen, aluminum, magnesium, and, in some cases, oxygen and nitrogen are also removed by vacuum extraction from the solid ingot, usually by induction heating.

Zone refining is used extensively in the purification of all of the metals covered in this survey. Floating zone melting by electron bombardment is widely used, while other methods such as arc-zone and induction zone melting are employed to a lesser extent. Those metals that exhibit a solid phase transformation such as the group IV elements can also be purified by displacement of a transformed zone. Some of the more significant developments in zone refining are the use of multiple zones, continuous and semicontinuous refining, float-zone refining in ultrahigh vacuum, and application of hollow-cathode heat sources.

Purification by the decomposition of a metal iodide on a hot filament or surface has been successfully applied to titanium, zirconium, hafnium, vanadium, niobium, and chromium. Work on the thermodynamic principles and phase equilibria underlying the decomposition of iodides has resulted in a better basic understanding of the decomposition process, especially for the zirconium iodide system.

All of the metals of groups IV and V plus chromium have been purified by electrolysis of the crude metal or scrap from fused salt mixtures, usually chlorides or fluorides. Electrorefining is particularly important in the preparation of high-purity vanadium. Likewise, experiments on ultrapurification by electrotransport have been reported for vanadium and zirconium. This specialized technique depends on the migration of impurities under the influence of an electric field at elevated temperatures. Purification of the bulk metal by sublimation is limited primarily to chromium, although purification of metallic salts, particularly the chlorides, often depends on a sublimation or distillation step prior to their use as a reactant salt in the reduction process.

Single Crystal Preparation

The availability of these metals in high-purity form together with their increased use in the aircraft, space, and nuclear programs has resulted in a demand for single crystals of various sizes, orientations, and purities for use in many different research studies. The groups V and VI elements do not undergo phase transformations and hence are quite readily prepared in single crystal form directly from the melt. Their high melting points and chemical reactivity, however, require the use of high-temperature furnaces and either vacuum or inert gas protective atmospheres. While there are a number of variations in the crystal growing techniques, most of them employ the zone melting principle, in which the liquid zone is maintained by electron-beam, arc, or high-frequency induction heating. Electron-beam heating is used most extensively because of the ease of obtaining the high melting temperatures of these metals under a high vacuum. This method offers the advantages of zone purification and vacuum extraction along with the growth of the monocrystals.

The Czochralski technique of pulling an oriented seed crystal from the melt has been successfully used to grow large molybdenum and niobium single crystals. Likewise molybdenum and tungsten crystals have been grown by decomposition or reduction of their chlorides in a hydrogen atmosphere onto a coarse-grained filament.

The group IV elements exhibit phase transformations which eliminate or at least complicate the use of any of the above