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BOOK REVIEWS

CHEMICAL BONDING AND SPECTROSCOPY IN MINERAL CHEMISTRY. Edited by Frank J. Berry and David J. Vaughan. Chapman and Hall, London and New York, 1985. 325 pages. $73.00.

This book consists of eight review chapters, each written by a well-known investigator, on the applications of spectroscopy and theoretical electronic structure calculations to minerals. The techniques covered include X-ray absorption and photoelectron spectroscopy (D. S. Urch), optical absorption spectroscopy in the ultraviolet, visible, and near-infrared (R. G. Burns), Mössbauer spectroscopy (A. G. Maddock), electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectroscopy (W. R. McWhinnie), and luminescence spectroscopy (G. Walker). Two chapters (by J. Tossell and D. J. Vaughan) describe the applications of theoretical electronic structure calculations, primarily using the "cluster molecular orbital" approach to minerals. Finally, there is a chapter by F. J. Berry on the applications of spectroscopic techniques to the study of mineral surfaces. Unfortunately, there is no chapter on the relatively new spectroscopic techniques that exploit synchrotron radiation (EXAFS and EXANES). A more serious omission is the absence of a chapter on vibrational spectroscopy (infrared and Raman) and its applications to minerals and glasses. Indeed, vibrational spectroscopy can often give much more information on bonding and crystal chemistry than the techniques presented. The book, however, is much slanted toward transition metal–bearing minerals and, in this regard, the techniques presented are the most important.

The chapters on spectroscopy all have a similar format: namely, to present an introductory description of the theory and practical aspects of the spectroscopic technique followed by several examples of its application. The discussions of the theory behind each experimental method are all quite good. Readers who have completed a typical undergraduate quantum chemistry course should have no difficulty understanding any of the material in the text. Those without such a background will probably find a few sections hard (if not impossible) to follow yet, overall, should find the discussions quite accessible. I could not find any significant errors in any of the chapters, at least in those areas where I felt competent to judge.

There is not a great deal of discussion regarding how the applications of spectroscopy and quantum chemistry to minerals ultimately relates to problems in the Earth sciences. Moreover, the mineralogical applications surveyed are, in several instances, very much out of date. Indeed, for the most part, no applications done since 1982 are reported. None of the chapters provides a comprehensive bibliography of mineralogical applications because, as stated in the preface, the purpose of the volume is not to give a detailed review of applications. Still, such a bibliography would be very useful to keep track of the large growth in "mineral physics" research in the past few years. Moreover, a great deal of mineral spectroscopy is reported outside of the mineralogical literature and, as such, can often go unnoticed by the nonspecialist.

The first chapter, by Tossell, gives an overview of the currently used techniques in computational quantum chemistry that are being applied to minerals. Tossell's chapter is clearly meant for the nonspecialist in quantum chemistry, and his emphasis is to present results rather than the theory behind the methods. Although minerals are solids, there has been little use of band theory to describe their electronic structures. Instead, the predominant approach is to use a cluster molecular orbital formalism. *Ab-initio* and the less-sophisticated CNDO methods applied to finite clusters are shown to accurately predict bond lengths and coordination site geometries. However, because the *ab-initio* methods are based on Hartree-Fock theory, the orbital energies obey Koopman's theorem. As such, they don't give a good description of electronic spectra. Moreover, *ab-initio* techniques are not easily applied to transition-metal systems, and their use has been restricted primarily to clusters containing first-row elements. Some of these shortcomings are remedied by using the SCF-Xα-SW method, which can easily handle transition-metal systems and usually gives an accurate prediction of the electronic transition energies observed in the spectra of minerals. On the other hand, the SCF-Xα-SW method appears to give a poor description of how the total energy of a cluster varies with its geometry and, as such, cannot accurately predict bond lengths and bond angles. Tossell also reviews some of the applications of the modified electron gas (MEG) method to mineral systems.

The chapter on X-ray spectroscopy and chemical bonding in minerals by D. S. Urch shows how the x-ray emission (XES) and X-ray photoelectron (XPS) spectra can be used to directly probe the electronic structures of minerals and derive information about chemical bonding. There is not much attempt to correlate the experimental results with theoretical calculations such as those discussed by Tossell in the previous chapter, however.

The chapter by R. G. Burns explains how the optical spectra of minerals can be used to characterize the crystal chemistry of transition-metal cations. Burns goes on to show how electronic transitions in minerals are important to the physics and chemistry of the Earth's interior (e.g., high-spin to low-spin transitions of Fe^{2+}, blocking of radiative heat flow by Fe^{2+}). Finally, a short section illustrates some applications of electronic spectra to the determination of planetary-surface mineralogies by spectroscopic remote-sensing techniques. Burns's chapter is especially laudable in that he shows how an understanding of the electronic structures of minerals is important to many problems in the Earth and planetary sciences.

G. Walker's chapter on luminescence presents a readable account of the theory and a description of cathodoluminescence and spectral (emission spectroscopy and luminescence excitation spectroscopy) techniques. Thermoluminescence is not discussed. The examples presented are mostly concerned with the Mn^{2+} center in silicates and carbonates since that is the most common luminescence center in minerals. A description of luminescence resulting from defect centers in quartz is also presented.

A. G. Maddock's chapter on Mössbauer spectroscopy provides an excellent and concise account of the theory behind the technique and goes on to review some of the applications of Mössbauer spectroscopy to the determination of the site occupancies and oxidation states of Fe in minerals. Such routine analytical applications of the technique are the most important to mineralogists. One of the more interesting applications of Mössbauer spectroscopy, however, is understanding the magnetic structures of minerals. A great deal of work has now been done on measuring the magnetic hyperfine fields at low temperature to determine the nature and temperature of magnetic ordering. Such studies are important to understanding the origins of low-temperature heat-capacity anomolies in Fe-bearing silicates. Unfortunately, none of this material is reviewed. On the other hand, a short account describing the effects of superparamagnetism in iron oxides is presented that is very important to the applications of Mössbauer spectroscopy to sediments and soils. Finally, the chapter has a section on electron hopping in mixed-valence Fe minerals and its observation using the Mössbauer effect. Several of the conceptual errors that are in the literature of mixed-valence minerals show up in the discussion presented here. These are not serious, however.

The chapter by W. R. McWhinnie on electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectroscopy also gives an excellent account of the theory behind the techniques. The applications of ESR spectroscopy that are reviewed are primarily concerned with transition-metal cations in clay minerals and zeolites. A very important use of ESR spectroscopy is the characterization of radiation-induced defects in minerals; however, this topic is not discussed. The applications of NMR spectroscopy discussed are also restricted to clay minerals and zeolites. Few of the many applications of NMR to other minerals and glasses that have been done in the past few years are reviewed.

The chapter by D. J. Vaughan discusses the electronic structures of sulfides and oxides. The use of the SCF-Xα-SW molecular orbital method on MO_n and MS_n clusters to determine the electronic structures of sulfides and oxides is elaborated upon. Most of the electronic-structure calculations described in this chapter are the pioneering applications of the SCF-Xα-SW method to minerals done by Tossell and Vaughan in the 1970s. In my opinion, the use of simple MS_n clusters has been taken to the limit when applied to the crystal chemistry of sulfides, and it is clear that electronic structure calculations using much larger clusters need to be done if phenomena such as metal-metal bonding and d-band formation are to be properly addressed.

The final chapter by Berry is on the characterization of mineral surfaces by X-ray photoelectron, conversion electron Mössbauer, and Auger electron spectroscopy. This chapter is the most novel, and the discussion presented is much needed. The study of mineral surfaces will undoubtedly be a major effort in the future owing to the potential relevance to geochemistry.

Prior to this book the two-volume work by A. S. Marfunin was the primary survey of experimental and theoretical investigations on the quantum chemistry and electronic spectroscopy of minerals. Unfortunately, Marfunin's books suffered from a poor English translation and numerous typographical errors. The emphasis was on work done in the USSR; many of the important papers published in the United States and Great Britain were ignored. *Chemical Bonding and Spectroscopy in Mineral Chemistry,* therefore, is a welcome addition insofar as it presents a much more readable account of the important spectroscopic techniques used in mineralogy. Also, the chapters by Tossell and Vaughan give a much more current account of the theoretical approaches being used to determine the electronic structures of minerals. One problem, however, is that the book is very expensive, and as such, it probably won't show up in many personal libraries.

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GEOLOGY AND GEOCHEMISTRY OF EPITHERMAL SYSTEMS (Reviews in Economic Geology, Volume 2, J. M. Robertson, Series Editor). Edited by B. R. Berger and P. M. Bethke. PUBCO, Reviews in Economic Geology, P.O. Box 637, University of Texas at El Paso, El Paso, Texas 79968-0637, U.S.A., 1985. 298 pages. $16.00.

This volume is the second in the Reviews in Economic Geology series of the Society of Economic Geologists. These books are refined versions of text material accompanying "short courses" sponsored annually by the society. *Geology and Geochemistry of Epithermal Systems* lives up to the high standard set by Volume 1 in this series (*Fluid-Mineral Equilibria in Hydrothermal Systems*) and is a logical follow-up to the subjects addressed in the previous volume. The authors in Volume 2 are acknowledged experts in their respective fields and have contributed to a uniformly high-quality product that will reach a wide audience.

As stated in the Preface, the volume "is an attempt to provide a synthesis of the current state of geological and geochemical knowledge of epithermal precious-metal systems." This goal is reached through 12 chapters that begin with a review of hydrothermal systems in general and terrestrial magmatic-hydrothermal systems in particular. R. W. Henley then outlines some of the chemical and physical requirements for ore formation in epithermal systems. The chapter does a good job setting the scene for what follows. Henley and K. L. Brown provide a practical guide to thermodynamics and geothermal fluids in chapter 2. This is a distillation of material presented in much greater detail in Volume 1 of the series. Exercises scattered throughout the chapter provide the dedicated reader with examples of how to make some of the calculations; providing more of the answers would, however, have been helpful as the exercises are cumulative.

Chapters 3 and 4 describe the behaviors of silica and carbonate, respectively, in hydrothermal systems. R. O. Fournier clearly and simply addresses the cause and effect of silica-solubility changes in the body of chapter 3 and provides quantitative data and equations as an appendix. In chapter 4 he presents a much more mathematical treatment that relies on Volume 1 in the series for many of the equations. The more rigorous approach is necessary as anyone who has worked through "simple" carbonate equilibria problems is painfully aware. Together, these two chapters provide critical data on some of the most ubiquitous gangue minerals found in epithermal ore deposits.

In chapter 5, R. J. Bodnar, T. J. Reynolds, and C. A. Kuehn provide an excellent review of fluid phase equilibria in fluid inclusions from epithermal environments. Their very lucid and cautionary chapter describes what the careful inclusionist can learn and further provides several examples of how observations of inclusions can be interpreted to yield the most information. The examples show applications of a powerful computer program that will "soon" be available to workers in this field (Bodnar, pers. comm., 1986). The chapter should be required reading for all fluid-inclusion workers, not just those studying epithermal ores.

Chapter 6 is a review of the systematics of light stable isotopes by C. W. Field and R. H. Fifarek. The first half of the paper is a general introduction that suffers somewhat from a lack of clarity and an over-reliance on a secondary source (Friedman and O'Neil, 1977) for references to fractionation equations. This would not be necessarily bad except that the secondary source is becoming outdated and unfortunately contains numerous typographical and drafting errors to trip up the user. The second half of this chapter extensively reviews data on epithermal ores and provides an in-depth derivation of quantitative water-rock ratio equations.

The emphasis in the second half of the volume changes from the tools, to the deposits themselves. D. O. Hayba, P. M. Bethke, P. Heald, and N. K. Foley describe two main types of volcanic-hosted epithermal precious-metal deposits. These are an adularia-sericite type and an acid-sulfate type distinguished primarily on the basis of vein and alteration minerals. This general treatment is followed by a detailed example of each type, Creede and Summitville, respectively. The review and synthesis of the voluminous literature on the classic Creede deposit are by themselves worth the price of the book. The chapter closes by addressing in more detail the acid-sulfate type of alteration, as it is poorly documented in the literature compared to "porphyry-style" alteration.

W. C. Bagby and B. R. Berger provide a lengthy review of the economically important sediment-hosted disseminated precious-metal deposits in the western United States. They define jasperoidal- and Carlin-type subsets with both gold-rich and silver-rich endmembers and then give examples of the three most important endmember types. The paper highlights the substantial limits of our understanding of the absolute origins of these deposit types but concludes that, from a practical standpoint, we can efficiently explore for these lower-grade, large tonnage ores.

Chapters 9 and 10 provide data on trace-element patterns in epithermal deposits and hot-spring–type deposits, respectively. M. L. Silberman and B. R. Berger recognize three important subtypes (in contrast to Hayba et al., chapter 7)—quartz-adularia low-sulfur bonanza type, quartz-alunite high-sulfur bonanza type, and a hot-springs type. The Bodie and Paramount districts of eastern California are then used as case studies to point out practical keys to mineralization. The following paper (Berger and Silberman) presents data for several important hot-springs–type ore deposits, and the authors conclude that local conditions are key in explaining details of mineralization in specific deposits.

M. H. Reed and N. F. Spycher present a computational approach to modeling changes that occur during boiling and mixing in the near-surface environment. They compare the effects of boiling vs. cooling in a vein system and show how repeated self-sealing and breaking of a silica cap can cause significant shifts in precipitated sulfide and silicate assemblages, pH, gas fraction, and mole percent CO_2. The quantitative understanding of partitioning during boiling allows Reed and Spycher to predict that hot-springs gold deposits can result from sulfide-deficient, low-salinity boiling fluids whereas base-metal-vein gold deposits can form from sulfide-excess, high-salinity boiling fluids. Fluid-inclusion data are consistent with this distinction. The final portion of the chapter considers ways in which the boiling fluids and groundwater can interact to cause alteration and ore deposition. In total, the chapter provides a welcome quantification of observations that many geologists have made in the field and laboratory.

S. S. Adams provides a complete change of emphasis in the final chapter. Adams discusses the use of geologic information in the development of exploration strategies and derives what he refers to as a "data-process-criteria model" which considers geologic information, an awareness of human, political, and corporate factors, and ore-deposit models. Adams demonstrates how one would model epithermal deposits, using this approach, to facilitate future exploration. The chapter provides an interesting practical link from the purer science of the first 11 chapters to the real world of the corporate or exploration geologist.

This volume does not attempt to be either the final word on or a comprehensive treatment of epithermal ore systems. Most of the loose ends (e.g., no discussion of telluride ores, the hydrology of near-surface fluid flow, or ties to deeper porphyry-type systems) are caused by the lack of a suitable data base. I have no reservations about recommending this book to all economic geologists, geochemists, petrologists, and explorationists. The tools and explanations provided in the first half of the volume are of use to both novice and experienced geologists irrespective of immediate interest in the epithermal environment. I found this book eminently informative, readable, and thought-provoking; it certainly provides the framework of current understanding and a guide to future exciting research in these important ore types.

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NOTICES

New recommended values of the fundamental physical constants for international use

Chemists, physicists, engineers, and others in science and technology have a new, more accurate set of values for the fundamental constants now that work is completed on the *1986 Adjustment of the Fundamental Physical Constants.* The 1986 adjusted values are recommended by the Committee on Data for Science and Technology (CODATA), an interdisciplinary, scientific committee of the International Council of Scientific Unions with headquarters in Paris. The 1986 CODATA report, which gives the new set of recommended values, is the first revision of the 1973 CODATA report that established the first internationally adopted set of values.

The adjustment includes the new definition of the meter in terms of the distance traveled by light in a given time, measurements linking atomic lattice spacings to optical wavelengths that make possible significant improvement in the determination of the Avogadro constant, and measurements of the quantization of the electrical conductance in certain semiconductor devices—the quantum Hall effect—discovered by Nobel laureate Klaus von Klitzing in 1980.

Although there are changes in all of the 1973 recommended values, the major changes include decreased values for the Planck constant, the elementary charge, and the electron mass and increased values for the Avogadro constant, the Faraday constant, and the Josephson frequency-voltage ratio. Most importantly, throughout the 1986 set of recommended numerical values, the uncertainties are now typically about 10 times smaller than those in the 1973 set.

Copies of the *1986 Adjustment of the Fundamental Physical Constants,* CODATA Bulletin 63, may be purchased in North America for $15 prepaid from Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A. Elsewhere, the bulletin may be obtained from Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, United Kingdom.

1987 Gordon Research Conference

The 1987 Gordon Research Conference on "Atomistic Approaches in Inorganic Geochemistry" will be held August 17–21, 1987, at the Proctor Academy, Andover, New Hampshire. Applications or further information may be obtained from Alexander Cruickshank, Gordon Research Conferences, Gordon Research Center, University of Rhode Island, Kingston, Rhode Island 02881-0801, U.S.A. (phone, 401-783-4011 or 401-783-3372).

See also the notice on p. 447