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BOOK REVIEWS

Reviews in Mineralogy and Geochemistry, Volume 39, *Transformation Processes in Minerals*, edited by S. A. T. Redfern and M. A. Carpenter, The Mineralogical Society of America, Washington, D.C., 2000, 361 pp., US $32 (ISBN 0-939950-51-0).

September 2000 saw me in Cambridge, England, for the Mineralogical Society of America (MSA) short course on Transformation Processes in Minerals, the first MSA short course to be held outside North America. Calling in to the Cambridge Department of Earth Sciences 2 d before the course commenced, I was shown a large box of books, Reviews in Mineralogy and Geochemistry volume 39, hot off the press and ready to be handed out to the course participants. An impressive effort by organizers, lecturers, and printers to have this book ready in time!

I remember enjoying the one and a half days of lectures, and afterward the experience of being punted up (or was it across?) the river Cam by eminent earth scientists, umbrellas being fashionable if not de rigeur. Notwithstanding the conditions, the strawberries and champagne supplied upstream helped to make this a highlight event. All in all, a very pleasant few days in Cambridge, and still back home in time for the Olympics.

Much water has passed under the bridge since that course last September, specifically in Cambridge, where the Cam burst its banks in a once-every-300-yr flood. My recollection of the lectures has faded, and I think now I can read and review the book not as an adjunct to the lectures but as a work in its own right.

The book, *Transformation Processes in Minerals*, comprises 12 chapters of approximately equal length, corresponding to the 12 lectures presented at the Cambridge course. The focus of the first seven chapters is on the various kinds of phase transitions occurring in common, or at least popular, minerals. There follow four chapters describing, briefly, some less familiar techniques for the investigation of phase transitions. The final chapter, "Radiation-Induced Amorphisation," describes structural changes of a somewhat different kind. The reader would benefit by some previous knowledge of X-ray crystallography and the crystal structures of minerals, as well as previous exposure to the Landau theory of phase transitions such as that described in Salje's (1993) text.

The headings of the chapters are reproduced below, together with a few lines of additional description on each.

- "Rigid Unit Modes in Framework Structures," by M. T. Dove, K. O. Trachenko, M. G. Tucker, and D. A. Keen. Silicate minerals, although constructed from nearly rigid tetrahedra, show considerable flexibility nevertheless. The rigid unit modes (of vibration) provide an account of diffuse scattering at higher temperatures where such modes are dynamic, and of the structural transitions that occur when these modes are frozen in. The theory provides insight into negative thermal expansion as occurs in ZrW_2O_8.
- "Strain and Elasticity at Structural Transitions in Minerals," by M. A. Carpenter. The coupling between strain and the (Landau) order parameter permits the study of phase transitions through their effect on lattice parameters. This coupling helps to ensure order is long range, a condition for Landau theory to apply. Transition temperatures (or pressures), and the nature of the transition, can both be dramatically affected. Elastic constants are affected by the strain/order parameter coupling, and elastic constant anomalies tend to be larger than those in the strain.
- "Mesoscopic Twin Patterns in Ferroelastic and Co-elastic Minerals," by E. K. H. Salje. Twin boundaries are important in ferroelastic materials—indeed, ferroelastic switching is controlled by the movement under stress of domain walls. Salje describes careful X-ray studies of twin walls in $LaAlO_3$ and transmission electron microscopy studies in a number of other minerals. The intersection of a twin boundary with a surface is an object of particular interest, for example as a chemically active site. The analysis of this object leads to interesting new possibilities, such as the study of twin walls by atomic force microscopy investigations at the crystal surface.
- "High-Pressure Structural Phase Transitions," by R. J. Angel. The applicable Landau expansion is analogous to that for temperature-induced transitions but different in detail. Spontaneous strain can be determined from lattice parameter measurements, although such measurements in situ under pressure are difficult, and in extrapolation of the parameters of the high-symmetry phase, the nonlinear dependence of lattice parameters with pressure must be addressed.
- "Order–Disorder Phase Transitions," by S. A. T. Redfern. The matter of cation order–disorder in minerals involves a balance between energy (favors ordering) and entropy (favors disorder) terms. Both Bragg-Williams and Landau descriptions are discussed. Many minerals showing high-temperature structural transitions also allow cation ordering, in which case the coupling of order–disorder (order parameter $Q_{\text{o-d}}$) via its strain field to the displacive changes (order parameter Q) becomes a matter of special interest. Such coupling has many implications, including the possibility, in favorable cases, of monitoring the long-range cation order through measurement of strain.
- "Phase-Transitions Induced by Solid Solutions," by P. J. Heaney. Changes in chemical composition can induce phase transitions in much the same way as changes in temperature or pressure. A simple extension of Landau theory suggests that transition temperatures should depend linearly on composition, while the character of the transition (e.g., second-order or tricritical) might also be composition dependent. Case studies include the technologically important materials lead zirconate-titanate (PZT) and stabilized zirconia, cuproscheelite–sanmartinite solid solutions, and substitutions in feldspars where cation ordering can promote framework collapse.
- "Magnetic Transitions in Minerals," by R. J. Harrison. The author describes the interactions driving magnetic ordering and the various magnetic arrangements which result. Cation ordering influences magnetic properties in many ways—magnetic transition temperatures, saturation values of magnetization, even the nature of the magnetic structure itself—making it possible in favorable cases to infer cation ordering from measurements of magnetic properties. As a scientist without background in the earth sciences, I was intrigued by the material on self-reversed thermoremnant magnetization and the problems this has posed for the history of the Earth's magnetic field.
- "NMR Spectroscopy of Phase Transitions in Minerals," by B. L. Phillips. Nuclear magnetic resonance is sensitive via chemical shifts and nuclear quadrupolar splittings to short-range structure, including site symmetry, and low-frequency dynamics. The resolution afforded by magic angle spinning (MAS) is critical in many applications. Several applications are described. Measurements of (time-averaged) site symmetries and bond angles in (cubic) β-cristobalite are consistent with the occurrence of rigid unit modes. Peak splitting in ^{29}Si MAS-NMR spectra from anorthite, $CaAl_2Si_2O_8$, has been used to follow the order parameter associated with a phase transition in this mineral. The sensitivity of chemical shift in ^{29}Si MAS-NMR to the occupants of neighboring tetrahedra makes this a powerful tool for studying Si/Al ordering in framework aluminosilicates.
- "Insights into Phase Transitions from Mössbauer Spectroscopy," by C. A. McCammon. The Mössbauer effect, like NMR, is sensitive to the local environment at the relevant nucleus. Most studies involve the Mössbauer nucleus ^{57}Fe. The key parameters of the Mössbauer spectrum are isomer (chemical) shift, nuclear quadrupolar splitting, and magnetic hyperfine splitting. The instrumentation is relatively straightforward, and the capacity for measurements in situ under conditions of varying temperature, pressure, and magnetic field is

considered an advantage. A study of the incommensurate to normal transition in Fe-doped åkermanite is described in detail.

- “Hard Mode Spectroscopy of Phase Transitions,” by U. Bismayer. Many phase transitions are induced by the freezing in of a particular mode of vibration, the “soft mode.” The structural changes also affect the other modes, the “hard modes,” and these can be investigated by infrared and Raman spectroscopies. Phonon coordinates are coupled with the order parameter, and the theory becomes complicated. It is found that Raman intensities depend on the square of the order parameter below the transition but reflect (precursor) short range order above. Examples of lead phosphate and titanite are discussed. The 496 K transition in synthetic titanite is thought to involve correlated displacements of the Ti from the centers of the TiO_6 octahedra, and these persist over a short range above the transition. The transition is largely washed out in natural titanite because of substitution of Ti by Fe and Al impurities.
- “Synchrotron Studies of Phase Transitions,” by J. B. Parise. After a brief overview, the author focuses on X-ray diffraction studies at synchrotrons and the practicalities of the same. Techniques include diffraction from single crystals and microcrystals, and powder diffraction of both angle- and energy-dispersive varieties. The time-resolved study of K^+/Na^+ exchange in certain zeolites is an interesting application. The author commends the capabilities at synchrotrons for simultaneous in situ measurements on phase transitions, and concludes that “measurement of the properties most critical to interpreting the earth are no longer in the realm of the possible, but are in the process of passing into the routine and user friendly.”
- “Radiation-Induced Amorphization,” by R. C. Ewing, A. Meldrum, L. M. Wang, and S. X. Wang. This chapter stands apart from the rest insofar as amorphization is not something to which Landau theory is applied. Amorphization is, however, a serious concern in the development of waste forms for actinides. The chapter serves as a useful introduction to radiation damage effects in solids, to the various means to study these (examination of naturally radioactive minerals, actinide doping, and charged particle irradiation), and to the radiation response of some common minerals. Minerals respond differently, not so much because of differences in damage caused, but more as a result of differences in the rates at which such damage is repaired. There are applications in geology as well as in nuclear waste forms—for example, it is sometimes possible to estimate the age of radioactive zircon from the amount of damage it shows.

To summarize, the book provides an excellent overview of the current state of research on phase transitions in minerals, especially as regards their description by Landau theory. As the first in the series published jointly by the Mineralogical Society of America and the Geochemical Society, it is a worthy volume. The chapters are well organized, and there are numerous literature references for the reader who craves further detail. The book is a well-presented paperback and adequately illustrated, although there are some problems that I attribute to a combination of word processor glitches and a tight deadline—missing symbols, repeated lines, and in one case, apparently missing lines. This volume should be of interest to all concerned with phase transformations in minerals, and also to those (such as myself) without background in mineralogy but with interests nevertheless in phase transitions and the application of Landau theory to their description. At only US$32—less to members of the MSA—it is very good value indeed.

REFERENCE

Salje E. K. H. (1993) *Phase Transitions in Ferroelastic and Co-Elastic Crystals.* Cambridge University Press.

Australian Nuclear Science and Technology Organisation Menai New South Wales 2234 Australia

Christopher J. Howard