Structural Aspects of Phase Transitions in Inorganic Crystalline Solids

Todd A. Marquart Literature Seminar November 15, 1990

Important physical properties of solids are directly related to the capacity of these materials to undergo phase transitions, resulting in change of crystal morphology, during their manufacture or use. New properties are attainable in materials by exploiting this morphology change. Insight into the physical basis of phase transition processes is available through Landau theory.

Several important materials such as zeolites, perovskites, memory metals and superconductors undergo phase transitions. Zeolite ZSM-5 has been shown to undergo a phase transition from a monoclinic structure to an orthorhombic structure at approximately 40°C [1,2]. Because this material is grown at elevated temperatures where it exists as the orthorhombic phase, severe twinning occurs when it is cooled to the monoclinic phase at room temperature. This twinning makes a detailed structural study of ZSM-5 difficult. The perovskite $BaTiO_3$, an important ferroelectric material, undergoes a thermally induced tetragonal to cubic transition at 125°C accompanied by a transition from ferroelectric to paraelectric [3]. TiNi, a material used to join titanium hydraulic tubing in the Grumman F14 Navy jet fighters, undergoes a monoclinic to cubic transition which is directly linked to its most interesting property, that of shape memory [5]. The property of superconductivity is closely related to the structure of the material. $Zr_{1-x}S$ is a low-temperature superconductor for which the low-temperature structure was not known until fairly recently [11,12,17]. From the aforementioned examples it is clear that the structure and properties of materials are directly linked.

A phase transition of one material may be used to engineer different properties into other materials such as is done in transformation toughening. Here, ZrO_2 is introduced into an Al_2O_3 matrix, a brittle material in its pure form, to make the ceramic more shock-resistent [4]. In this application the ZrO_2 acts as a toughener by absorbing stresses incurred upon the matrix by undergoing a stress-induced phase transition.

Due to the important and often difficult task of understanding phase transitions, it is fortunate that a strong theoretical framework exists, the Landau theory [6-9] of symmetry and phase transitions. It is not uncommon for it to be very difficult, if not impossible, to unambiguously determine the structure of a solid which has undergone a phase transition due to resultant twinning and the low intensity of diffraction lines arising from superstructure. The use of Landau theory to clarify diffraction patterns has been very recently reviewed by H. F. Franzen [10].

The symmetry rules of Landau theory only apply to second-order phase transitions, which are necessarily continuous. First- and second-order transitions vary in that a transition in which there does not exist a region where both phases coexist in equilibrium is necessarily second-order. This property suggests that these transitions are strongly bound by symmetry. The main thrust of Landau's theory is that it is possible to expand the Gibbs free energy function in a Taylor series as a function of the order parameter, η, where η describes the overall extent of the distortion (in the case of an order-disorder transition, $\eta = 0$ implies a perfectly disordered structure and $\eta = 1$ describes a completely ordered structure).

$$G = G^\circ + \alpha\eta + A\eta^2 + B\eta^3 + C\eta^4 + \ldots$$

α must be zero at $\eta = 0$ for G to be a minimum at this point

$$G = G^\circ + A\eta^2 + B\eta^3 + C\eta^4$$

where A, B and C are functions of state variables. If B does not equal 0 by symmetry it is impossible for a second-order transition to occur except at isolated state points where B goes to zero by chance. Therefore, the Gibbs free energy function which describes a second-order transition is:

$$G = G^{\circ} + A\eta^2 + C\eta^4$$

where C has been taken to be positive (if C were less than zero the function would have to be expanded to the sixth order which necessarily leads to a first-order transition). A second-order transition occurs as A passes through zero at the transition point. It follows that for A to go to zero at a succession of points, A must correspond to a single irreducible representation. Because G must be the same for equivalent distortions it must be invarient under symmetry operations. Therefore, this function can be written as a function of invarient combinations of the basis functions which correspond to the transition. The basis functions which describe the transition are those which are symmetric to the symmetry operations retained and anti-symmetric to those which are lost. This function may be minimized to give possible space groups which can result from a second-order transition from some parent symmetry.

This approach along with experimental observations has been used in the examination of the defect NaCl structure of $Zr_{1-x}S$ [11,12], $Sc_{1-x}S$ [11], the oxides of Ni, Mn, Co and Fe [10,13-16] of which $Zr_{1-x}S$, $Sc_{1-x}S$, and others are low-temperature superconductors [17]. This technique has been used in numerous intermetallics with the CsCl parent structure such as RhTi [18,19], $NbRu_{1+x}$ [19], TaRu [20], AuCd [21], TiNi [21], $V_{0.54}Ir_{0.46}$ [23] and LiPb [21], several of which are related to memory metals. J. D. Corbett has recently used the theory to help explain the formation of unequal Zr-Zr bonds in ZrI_3 [22,24].

References

1. Van Koningsveld, H.; Jansen, J. C.; Van Bekum, H., "The Monoclinic Framework Structure of Zeolite H-ZSM-5. Comparison With the Orthorhombic Framework of as-Synthesized ZSM-5," *Zeolites*, **1990**, *10*, 235.

2. Klirowski, J.; Carpenter, T. A.; Gladden, F., "High Resolution Solid-State n.m.r. Studies of Temperature Induced Phase Transitions in Silicalite (Zeolite ZSM-5)," *Zeolites*, **1987**, *7*, 73.

3. Kittel, C., *Introduction to Solid State Physics*, 6th Ed., John Wiley & Sons, Inc.: New York, 1986.

4. Evans, A. G.; Cannon, R. M., "Toughening of Brittle Solids by Martersitic Transformations," *Acta Metall.*, **1986**, *34*, (5), 761.

5. Wayman, C. M.; Harrison, J. D., "The Origins of the Shape Memory Effect," *JOM*, **1989**, *41*, 26.

6. Landau, L. D.; Lifshitz, E. M., *Statistical Physics*, Pergamon Press: London, 1958.

7. Franzen, H. F., *Second-Order Phase Transitions and the Irreducible Representation of Space Groups*, Springer-Verlag: Heidelberg, 1982.

8. Franzen, H. F., *Physical Chemistry of Inorganic Crystalline Solids*, Springer-Verlag: Heidelberg, 1986.

9. Tolédano, J. C.; Tolédano, P., *The Landau Theory of Phase Transitions*, World Scientific: New Jersey, 1987.

10. Franzen, H. F., "Landau Theory of Symmetry-Breaking Transitions: A Basis for Classification of Diffraction Studies of Phase Behavior," *Chem. Mater.*, **1990**, *2*, 486.

11. Franzen, H. F.; Folmer, J. C. W., "Defect Ordering in Early Transition-Metal Sulfides with the NaCl-Type Structure," *J. Solid State Chem.*, **1987**, *51*, 396.

12. Kim, S. J.; Nguyen, T. H.; Franzen, H. F., "The Homogeneity Ranges, Order-Disorder Transition, and Structures of the Nonstoichiometric Monosulfides of Zirconium," *J. Solid State Chem.*, **1987**, *20*, 88.

13. Franzen, H. F., "Thermal Symmetry Breaking Transitions in NaCl-Type Solids," *J. Less-Common Met.*, **1989**, *146*, 229.

14. Rooksby, H. P., "A Note on the Structure of Nickel Oxide and Subnormal and Elevated Temperatures," *Acta Crystallogr.*, **1948**, *1*, 226.

15. Tombs, N. C.; Rooksby, H. P., "Structure of Monoxides of Some Transition Elements at Low Temperatures," *Nature*, **1950**, *165*, 442.

16. Willis, B. T. M., Rooksby, H. P., "Change in Structure of Ferrous Oxide at Low Temperature," *Acta Crystallogr.*, **1953**, *6*, 827.

17. Moodenbaugh, A. R.; Johnston, D. C.; Viswanathan, R.; Shelton, R. N.; Delong, L. E.; Fertig, W. A., "Superconductivity of Transition Metal Sulfides, Selenides and Phosphides with the NaCl Structure," *J. Low Temp. Phys.*, **1978**, *33*, 175.

18. Yi, S. S.; Chen, B. H.; Franzen, H. F., "Phase Transitions in RhTi," *J. Less-Common Met.*, **1988**, *143*, 243.

19. Chen, B. H.; Franzen, H. F., "High Temperature X-ray Diffraction and Landau Theory Investigation of Phase Transitions in $NbRu_{1+x}$ and RhTi," *J. Less-Common Met.*, **1989**, *153*, L13.

20. Chen, B. H .; Franzen, H. F., "Phase Transitions and Heterogeneous Equilibria in the TaRu Homogeneity Range," *J. Less-Common Met.*, **1990**, *157*, 37.

21. Franzen, H. F.; Chen, B. H., "Symmetry Breaking Transitions in CsCl-Type Solids," *J. Solid State Chem.*, **1990**, *88*, 247.

22. Lachgar, A.; Dudis, D. S.; Corbett, J. D., "Revision of the Structure of Zirconium Triiodide. The Presence of Metal Dimers," *Inorg. Chem.*, **1990**, *29*, 2242.

23. Chen, B.; Franzen, H. F., "A Second-Order Phase Transition in $V_{0.54}Ir_{0.46}$," *J. Less-Common Met.*, **1990**, *159*, 343.

24. Franzen, H. F., "Distortions in the D_{6h} Crystal Class to a x a$\sqrt{3}$ x c Orthorhombic Lattice," *J. Solid State Chem.*, **1990**, *85*, 173.