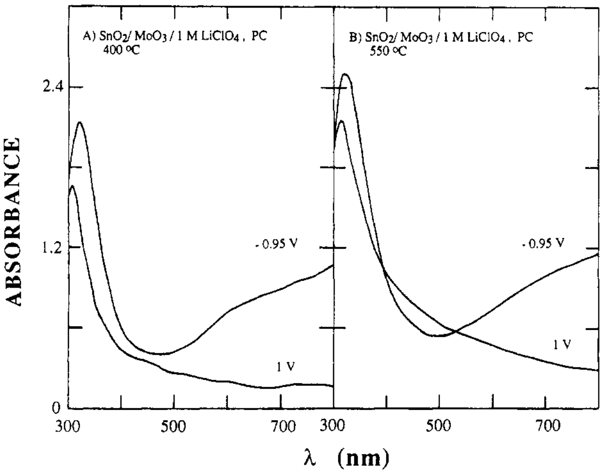

Figure 3. Absorption spectra of SnO_2/MoO_3 electrodes bleached at 1 V and colored at -0.95 V vs Ag/Ag^+ in 1 M $LiClO_4$, PC. Electrode prepared at 400 °C (A) and 550 °C (B).

films prepared at 400 and 550 °C are shown in Figure 3. The films are colorless when potential positive of 1 V vs Ag/Ag^+ is applied to the MoO_3 electrode. Reduction of the film at negative potential such as -0.95 V vs Ag/Ag^+ resulted in the formation of deep blue Li_xMoO_3. The evaluation of the electrochromic performance of a material involves the determination of the coloration efficiency and the switching time. The coloration efficiency, evaluated from the slope of the graph of the optical density versus the charge injected,[18] has been measured at 634 nm. For 0.15-μm-thick film, coloration efficiencies of about 30 and 10 $cm^2\ C^{-1}$ have been obtained for films heated at 400 and 550 °C, respectively. The coloration effiency of the film prepared at 400 °C is slightly lower than the values reported in the literature for molybdenum trioxide obtained by annealing of molybdenum black.[19] However, it should be noted that a different electrolyte was used in the latter study. The switching time, defined as the time necessary to record a variation of 0.3 unit of optical density,[19] for MoO_3 films prepared at 400 and 550 °C are in the order of 50 and 500 s, respectively. The data presented above and in Figure 3 indicates that the films prepared at 400 °C show a better bleaching and better electrochromic performances than those prepared at 550 °C. This is presumably related to an enhancement of reflected light at higher temperature due to increasing crystallization. Further, the films prepared at 550 °C have a white powder appearance, while films heated at 400 °C are clearly more transparent.

This paper has described the preparation of molybdenum trioxide thin film by an electrochemical/thermal process. Our preliminary results on the characterization of these deposits are also given. Current work in our laboratory aimed at a more detailed characterization of the MoO_3 thin films is underway and will be reported elsewhere. Future work will also be directed toward a comparison of the electrochromic properties of molybdenum trioxide prepared by various methods to identify the more efficient material and toward the enhancement of the electrochromic switching characteristics of our MoO_3 thin films. Since it is well-known that the electrochromic properties of a material are related to the preparation technique,[20] it is worthwhile to evaluate this new preparation technique for the preparation of MoO_3 thin films.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (Operating grant), the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Nouveaux chercheurs), and the "Action Structurante" program of the Quebec Government for partial support. We thank Suzie Poulin of the Ecole Polytechnique in Montreal for XPS measurements and Raymond Mineau and Michel Preda of UQAM and SEM and X-ray diffraction measurements, respectively.

Registry No. MoO_3, 1313-27-5; MoS_3, 12033-29-3.

---

(18) Bange, K.; Gambke, T. *Adv. Mater.* **1990**, *2*, 10.

(19) Donnadieu, A.; Davazoglou, D.; Abdellaoui, A. *SPIE* **1988**, *1016*, 124.

(20) Machida, K.-I.; Enyo, M. *J. Electrochem. Soc.* **1990**, *137*, 1169.

Reviews

Landau Theory of Symmetry-Breaking Transitions: A Basis for Clarification of Diffraction Studies of Phase Behavior

Hugo F. Franzen

Ames Laboratory—DOE and Department of Chemistry, Iowa State University,
Ames, Iowa 50011

Received May 8, 1990

The appliation of the Landau theory of symmetry and phase transitions is reviewed. A number of recent applications that resulted in clarifications of confused or mistaken heterogeneous equilibria and structures are presented.

Introduction

There is a type of problem that arises in the study of the structure of materials for which the usual diffraction methods of structure determination are not well suited. The problem arises because a crystalline solid that occurs either in principle or in practice in some high-symmetry space group in some of its range of existence exists in a form of broken symmetry under the conditions of the

0897-4756/90/2802-0486$02.50/0

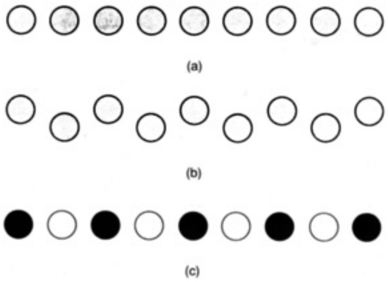

Figure 1. Symmetry-breaking transitions in a linear chain (b) displacive, (c) order–disorder. Note the loss of inversion and reflection symmetry, in (b) the reflection at the point midway between the atom sites and the inversion at the atom sites, while in (c) both are lost at the midway points.

diffraction experiment. The symmetry might be broken by a displacive transition, an order–disorder transition, or a transition that is a combination of these two types. The structural problems arise in part because such transitions frequently result in multiple twinning on a submicroscopic level, making it very difficult to obtain a single-crystal suitable for diffraction study, and in part because the changes in structure are frequently rather subtle, giving rise to small splittings of diffraction peaks (in a powder pattern) and/or weak superlattice reflections. Nonetheless, the understanding of such structural changes is important to the understanding of the chemistry of materials. On one hand such subtle structural changes are frequently associated directly or indirectly with interesting and useful property changes (metal to insulator, para- to ferroelectric, para- to antiferromagnetic, normal to superconducting). Therefore, it is fortunate that there exists a strong theoretical framework, the Landau theory of symmetry and phase transitions, that applies to the consideration of such transitions. The purpose of this review is to provide an introduction to this theory and its application.

The Theory

The Landau theory is described in the famous multivolume work of Landau and Lifshitz.[1] Later works providing tutorial details have appeared,[2] the most thorough of which is a recent book by Toledano and Toledano.[3] The theory applies to phase transitions that occur continuously, i.e., to symmetry breaking that occurs when a structure changes continuously. To envision such an event it is necessary only to consider a one-dimensional chain of atoms (Figure 1). If such a chain continuously distorts into a zigzag chain (i.e., if the distance of the atoms from the chain axis increases continuously, alternating in an up-and-down direction), then some symmetry is maintained (reflection through planes at the atom position and perpendicular to the chain, inversion through points midway between the atom positions) and some is lost (reflection through planes midway between the atom positions, inversion through the atom positions). Similarly if such a chain is occupied randomly in two different ways (atoms and vacancies, atoms of two different elements), then the average diffraction symmetry is broken if the two different entities order in an alternating fashion (e.g., if each site is, on the average 90% occupied and at some temperature the occupation along the chain, $0.9 + \delta$, $0.9 - \delta$, $0.9 + \delta$, $0.9 - \delta$, ..., changes with the continuous onset of $\delta \neq 0$). Transitions of this character can also occur in three-dimensional crystalline solids as observed in the NiAs-type to MnP-type transition[4] (Figure 2) and in the transition observed in $Y_{1-x}Se$[5] (Figure 3) from NaCl-type to a cubic superstructure with $a = 2a_{NaCl}$.

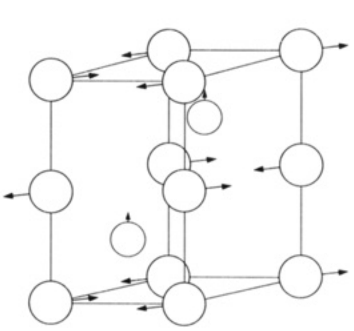

Figure 2. NiAs-type (hexagonal, $P6_3/mmc$) to MnP-type (orthorhombic, *Pcmn* (*Pnma* in the conventional setting)) phase transition. The hexagonal unit cell is shown. The orthorhombic unit cell has the approximate dimensions a_{hex} (short-face diagonal) $\times\ 3^{1/2}a_{hex}$ (long-face diagonal) $\times\ c_{hex}$.

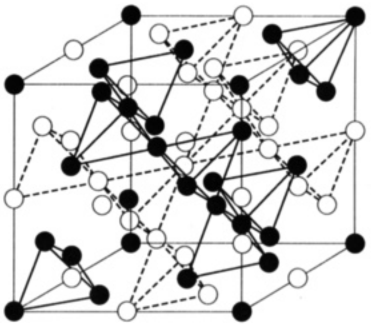

Figure 3. Cubic superstructure ($a = 2a_{NaCl}$, $Fd3m$) of the NaCl-type structure observed for $Y_{1-x}Se$. The substructure unit cell is a cube one-eighth the size of the substructure cell.

Such continuous symmetry-breaking transitions have four characteristics that were discovered by Landau. The first, which is obvious from the descriptions of the processes given above, is that the space group (or just the symmetry group if there is no space group as in the case of an incommensurate structure) with broken symmetry is a subgroup of the space group of the high symmetry form. This characteristic is not very restrictive, and therefore it is not of great utility. For example, the space group of the NaCl-type structure has subgroups with every cubic, tetragonal, orthorhombic, rhombohedral, and monoclinic type, and since, with loss of translational symmetry only, $Fm\bar{3}m$ is a nontrivial subgroup of itself, the subgroups of each type occur over and over again.

The second characteristic discovered by Landau is that such transitions can be characterized by an order parameter. For example, in the linear cases of Figure 1 it is possible to imagine a function $\Delta\rho$ that adds and subtracts particle density in the appropriate fashion. If ρ is the three-dimensional particle density function of the lower symmetry structure and $\rho°$ that of the higher symmetry structure, then

$$\rho = \rho° + \eta\Delta\rho$$

where η is the order parameter that determines the extent to which the transition has occurred. Such a particle density function in the order–disorder case would have the symmetry of $\cos \pi x$, where x is the coordinate along the

---

[1] Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Pergamon Press: London, 1958; Vol. 5.

[2] Franzen, H. F. *Physical Chemistry of Inorganic Crystalline Solids*; Springer-Verlag: Heidelberg, 1986.

[3] Toledano, J.-C.; Toledano, P. *The Landau Theory of Phase Transitions*; World Scientific: Teaneck, NJ, 1987.

[4] Franzen, H. F.; Haas, C.; Jellinek, F. *Phys. Rev. B* **1974**, *10*, 1248.

[5] Kim, S.-J.; Franzen, H. F. *J. Less-Common Met.* **1988**, *144*, 117.

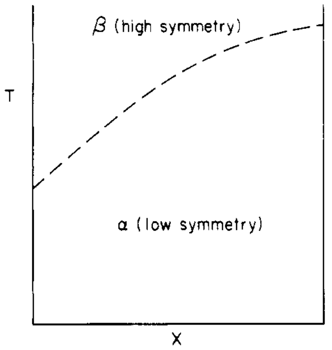

Figure 4. T–X phase diagram for a continuous transition. The low-symmetry structure continuously approaches the high-symmetry structure as the transition line is approached from below, and the loss of some symmetry occurs when the transition line is crossed from above.

chain in units of the interatomic spacing, i.e., $x = 0$ at one atom, $x = 1$ at the next, etc. Such a function is alternatively positive and negative at the atom positions and thus adds and subtracts "particle density" at alternating atom sites. The function $\Delta\rho$ is not equal to $\cos \pi x$ but can be approximated to any desired precision by the Fourier series which has the symmetry of $\cos \pi x$.

The theory as developed by Landau uses the order parameter as a basis for the expansion of the Gibbs free energy. Space limitations preclude a detailed development here; however, the theory is developed in detail in refs 1–3. The main idea is that $\Delta\rho$ can be expanded in a complete set of basis functions or, alternatively, that $\Delta\rho$ can be projected onto the basis functions for the irreducible representations of the high-symmetry space group. The first major conclusion that results stems from the fact that the basis functions for one irreducible representation will, because linear combinations transform in a closed fashion under symmetry operations, have equivalent thermodynamic consequences by symmetry. On the other hand, basis functions for a different irreducible representation will have different thermodynamic consequences. This leads directly to the conclusion that a continuous symmetry-breaking transition that occurs at a variety of temperatures as a function of some other variable, say composition (see Figure 4), corresponds to a single irreducible representation.

That is, $\eta\Delta\rho$ can be expressed as $\sum c_i\phi_i$, where the c_i's are coefficients and the ϕ_i's are basis functions for a single irreducible representation. The transition occurs when $\sum c_i^2$ changes continuously away from zero (so that $\eta\Delta\rho$ changes continuously away from zero). It is then useful to define $\gamma_i = c_i/(\sum c_i^2)^{1/2}$ (γ_i is a normalized c_i, i.e., $\sum\gamma_i^2 = 1$) and let $\eta = (\sum c_i^2)^{1/2}$ so that $c_i = \gamma_i\eta$, and

$$\eta\Delta\rho = \eta\sum\gamma_i\phi_i$$

or

$$\Delta\rho = \sum\gamma_i\phi_i$$

The second major conclusion from the theory is that it is necessary, if the transition is to occur continuously over a range of state variables (temperature and pressure or temperature and composition), that there be no third-order term in the Gibbs free energy. This is so because a third-order term necessarily leads to a coexistence of two phases, i.e., a first-order phase transition (Figure 5), whereas the absence of a third-order term permits a continuous breaking of symmetry (Figure 6). The occurrence of a third-order term in the G expansion is associated with a third-order combination of the ϕ_i's that transforms into itself under all symmetry operations of the group (i.e., a "third-order invariant"). Thus the existence of a third-order invariant combination of basis functions to which the transition corresponds means that the transition must proceed via two-phase coexistence and it cannot occur continuously. A third-order term that is not zero for symmetry reasons might vary with thermodynamic state so as to vanish at some isolated state point, in which case an isolated second-order transition could occur at this point.

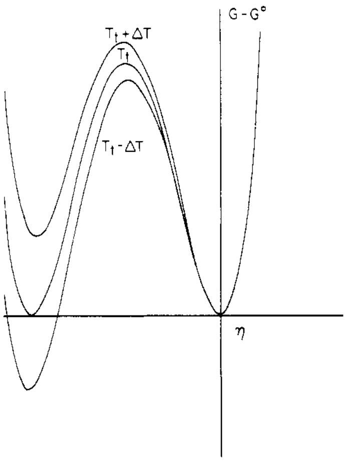

Figure 5. $G - G° = A\eta^2 + B\eta^3 + C\eta^4$ vs η for several temperatures where $A(T) > 0$ is taken to decrease with decreasing T. For the top curve $\eta^{eq} = 0$, for the bottom curve $\eta^{eq} \neq 0$, and for the middle curve $\eta^{eq} = 0$ *and* $\eta^{eq} \neq 0$, i.e., the high- and low-symmetry forms coexist. The high–low transition is therefore discontinuous.

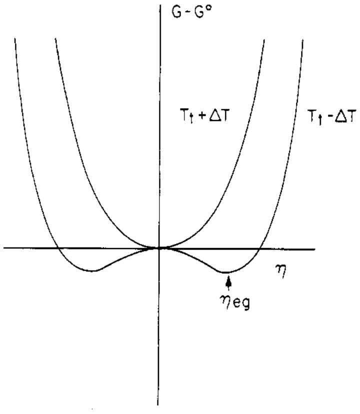

Figure 6. $G - G° = A\eta^2 + B\eta^4$ vs η for two temperatures. For the top curve $A(T) > 0$ and $\eta^{eq} = 0$, while for the bottom curve $A(T) < 0$ and $\eta^{eq} \neq 0$. A continuous symmetry breaking occurs when $A(T) = 0$.

A side benefit of the theory that provides one of its most useful results is that it yields the form of G as a function of the γ_i's, which can be minimized to yield structural results of significant utility. For example, it was found that defect zirconium sulfide ($Zr_{1-x}S$), an important superconducting solid,[6] has the NaCl-type structure above about 1200 °C but occurs with an ordered rhombohedral structure temperatures[7] (Figure 7). It was found the $Fm\bar{3}m \rightarrow R\bar{3}m$ meets all of the criteria discussed above. The function $\cos \pi(x + y + z)$ is symmetric with respect to the conserved translations (e.g., $\vec{a} + (\vec{b} + \vec{c})/2$, $\vec{b} + (\vec{a} + \vec{c})/2$, $\vec{c} + (\vec{a} + \vec{b})/2$) and antisymmetric with respect to lost translations (e.g., $\vec{a}$, $\vec{b}$, $\vec{c}$) and similarly symmetric with respect to 3-fold rotation about $\vec{a} + \vec{b} + \vec{c}$, inversion, etc.

---

[6] Moodenbaugh, A. R.; Johnston, D. C.; Viswanathan, R.; Shelton, R. N.; Delong, L. E.; Fertig, W. A. *J. Low Temp. Phys.* **1978**, *33*, 175.

[7] Kim, S.-J.; Nguyen, T.-H.; Franzen, H. F. *J. Solid State Chem.* 1987, *70*, 80.

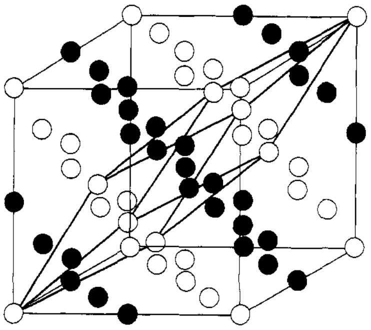

Figure 7. Rhombohedral ($R\bar{3}m$) ordered structure observed for $Zr_{1-x}S$.

Thus in this case $\Delta\rho$ has the symmetry of cos $\pi(x + y + z)$ which is a basis function of an irreducible representation of $Fm\bar{3}m$. This irreducible representation is, in fact, four dimensional, and a set of basis functions (corresponding to the four body diagonals of the cubic unit cell) is

$$\phi_1 = \cos \pi(x + y + z)$$

$$\phi_2 = \cos \pi(-x + y + z)$$

$$\phi_3 = \cos \pi(x - y + z)$$

$$\phi_4 = \cos \pi(x + y - z)$$

Since all four of these functions change sign under at least one symmetry operation of $Fm\bar{3}m$ (e.g., translation by $\vec{a}$ taking x into $x + 1$), there is no third-order invariant. There is a second-order invariant (as indeed there always must be), namely, $\sum\phi_i^2$, and there are three fourth-order invariants: $\sum\phi_i^4$, $\sum_{i\neq j}\phi_i^2\phi_j^2$, and $\phi_1\phi_2\phi_3\phi_4$, from which it follows that if

$$\rho = \rho^\circ + \sum c_i\phi_i$$

then to fourth order

$$G = G^\circ + A\sum c_i^2 + B_1\sum c_i^4 + B_2\sum_{i\neq j}c_i^2c_j^2 + B_3c_1c_2c_3c_4$$

where the A and B coefficients, which depend upon the state of the solid, are unknown. With $c_i = \gamma_i\eta$ and $\sum\gamma_i^2 = 1$

$$G = G^\circ + A\eta^2 + [B_1\sum\gamma_i^4 + B_2\sum\gamma_i^2\gamma_j^2 + B_3\gamma_1\gamma_2\gamma_3\gamma_4]\eta^4$$

Minimization of G subject to the restraint $\sum\gamma_1^2 = 1$ yields three possible solutions depending upon the magnitudes and signs of the coefficients, for example, $B_1 < 0$ and B_2 and $B_3 > 0$ yields a minimum for $\gamma_1 = 1$, $\gamma_2 = \gamma_3 = \gamma_4 = 0$. This solution has $R\bar{3}m$ symmetry. On the other hand, if B_1 and B_3 are positive and B_2 is negative, a minimum results for $\gamma_1 = \gamma_2 = \gamma_3 = \gamma_4 = {}^1/_2$ ($Fm\bar{3}m$ symmery, $a = 2a_{NaCl}$), whereas $B_3 < 0$ yields $\gamma_1 = \gamma_2 = \gamma_3 = -\gamma_4 = {}^1/_2$ ($Fd\bar{3}m$ symmetry, $a = 2a_{NaCl}$). The relationship between the coefficients and the symmetry is that ${}^1/_2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$ has space-group symmetry $Fm\bar{3}m$, while ${}^1/_2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$ has space-group symmetry $Fd\bar{3}m$, as can be verified by considering the effect of the symmetry operations upon x, y, z. The first solution is the one found for $Zr_{1-x}S$. Thus it has been demonstrated that the observed transition is consistent with Landau theory. The second and third solutions are then theoretical structures found by minimization of G. The third structure has been found for $Y_{1-x}Se$[5] (Figure 3). The allowed second-order transitions for the CsCl-type[8] and NaCl-type[9] structures and those to a $3^{1/2}ax$ a orthorhombic lattice[10] in the D_{6h} groups have been recently reported.

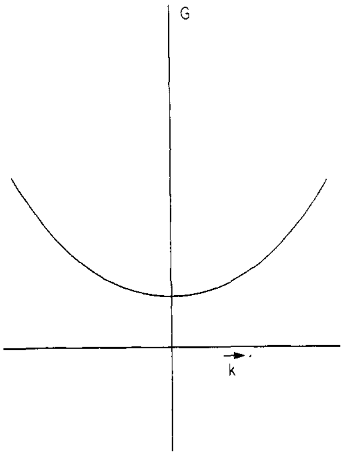

Figure 8. G vs $\vec{k}$ showing a minimum at the position fixed by a symmetry that results in G being an even function.

A technical point about space-group representations appeared implicitly in the preceding discussion, namely, the four basis functions mentioned, ϕ_1, ϕ_2, ϕ_3, ϕ_4, correspond to four periodicities; each doubles the period along a body diagonal, but in each case it is a different body diagonal. In solid-state physics such periodicities are dealt with through wave vectors, e.g., the reciprocal space vectors $\vec{k}$ that satisfy $\phi_i = \cos \vec{k}\cdot\vec{r}$ so that $\vec{k}_1 = \pi(\hat{i} + \hat{j} + \hat{k})/a$, $\vec{k}_2 = \pi(-\hat{i} + \hat{j} + \hat{k})/a$, etc. This means that the basis functions, and therefore the irreducible representations, are associated with specific wave vectors. In the case discussed above the wave vector for the $R\bar{3}m$ ordering is any one of the four wave vectors. The four $\vec{k}$ vectors form a set that is closed under all operations of the group, and such a set is called a star. The cubic orderings result from the superposition (with the appropriate signs) of all four functions and thus correspond to all of the wave vectors in the star. The Landau theory of the fourth and last characteristic of symmetry-breaking transitions involves the expression of the Gibbs' free energy as a function of the reciprocal space variables, i.e., the periodicities are treated as continuous variables. This is possible by considering reciprocal space to be continuously filled with points. This requires that there exist points corresponding to irrational periods and thus to incommensurate structures. Minima in the Gibbs free energy as a function of position in reciprocal space correspond to allowed stable structures, and such minima occur in two very different ways.[11] One kind of minimum is fixed by symmetry at special wave vectors, for example, a minimum in G vs $\vec{k}$ where $\vec{k}$ terminates at an inversion center will be fixed by symmetry because in this case $\vec{k} + \delta\vec{k}$ and $\vec{k} - \delta\vec{k}$ are equivalent by symmetry and therefore

$$G(\vec{k} + \delta\vec{k}) = G(\vec{k} - \delta\vec{k})$$

and thus G has an extremum fixed at $\vec{k}$ (Figure 8). If this extremum is a minimum, then the point represents a stable structure with a fixed periodicity. The other way that a minimum can arise is "by chance" at some point $\vec{k}$. In this case the position of the minimum in reciprocal space is not fixed but is free to vary with the thermodynamic state leading to a variable periodicity. Such a variable periodicity is the signature of an incommensurate structure. That is, if a minimum in $G(\vec{k})$ is not fixed by symmetry it will, in general, occur at $\vec{k}$ points that vary continuously with temperature, pressure, composition, magnetic field, etc. Thus the resultant structure will have a continuously

---

(8) Franzen, H. F.; Chen, B.-H. *J. Solid State Chem.*, in press.
(9) Franzen, H. F. *J. Less-Common Met.* **1989**, *146*, 229.
(10) Franzen, H. F. *J. Solid State Chem.* **1990**, *85*, 173.

(11) Haas, C. *Phys. Rev.* **1965**, *140A*, 863.

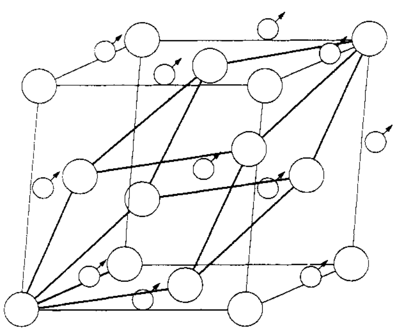

Figure 9. Rhombohedral (*R3m*) distorted structure proposed for NiO, FeO, and MnO.

varying period that for the majority of the $\vec{k}$ points is not commensurate with the period of the lattice of the undistorted structure. This can occur, for example, as the result of two uncoupled distances along a given direction, a helix of variable pitch uncoupled to the lattice or a set of crystalline domains with variable *average* period that is a nonintegral multiple of the sublattice period. In any of these cases the period is inherently incommensurate and is determined, from the point of view of Landau theory, by the location of the minimum in $G(\vec{k})$ at each state point.

On the other hand, the wave vectors at which extrema in G are fixed by symmetry are restricted to points of high symmetry in reciprocal space. The irreducible representations for which the extrema are fixed at the $\vec{k}$ points are those for which the product of the antisymmetric square representation and the vector representation do not contain the totally symmetric representation.[3] The four characteristics given by Landau theory for continuous symmetry breaking have been applied in a variety of cases as discussed below.

Applications

1. NiAs-Type = MnP-Type. This transition from hexagonal to orthorhombic ($P6_3/mmc$ to $Pnma$) can correspond to $\vec{k} = {}^1/_2, 0, 0$ (i.e., it can double the period in the x direction). There are, however, three wave vectors equivalent by symmetry (${}^1/_2, 0, 0; 0, {}^1/_2, 0;$ and ${}^1/_2, {}^1/_2, 0$ form a star), and thus three corresponding basis functions (each with the space-group symmetry of $Pnma$) are $\phi_1 = \cos(2\pi z)\sin(\pi x)$, $\phi_2 = \cos(2\pi z)\sin(\pi y)$, and $\phi_3 = \cos(2\pi z)\sin(\pi(z - y))$. The irreducible representation generated by these basis functions meets all of the conditions of Landau theory,[4] and a second-order phase transition yielding the MnP-type structure is possible in each of the three directions separated by 120°. It is of interest that a second possible minimum in G corresponds to all three periods superimposing yielding $P6_3mc$ symmetry with $a = 2a_{\mathrm{NiAs}}$. This hexagonal superstructure yields triangular clusters of the metal atoms and has been found for low-temperature NbS. A second feature of interest is that the transition does not occur through the intuitively appealing group–subgroup route of $P6_3/mmc \rightarrow Cmcm \rightarrow Pnma$. The transition from $P6_3/mmc$ to $Cmcm$ without loss of periodicity is not allowed by Landau theory because of the existence of a third-order invariant.[10] If a continuous transition were to occur to the C-centered orthorhombic cell, then the space group, to be consistent with Landau theory, would be noncentrosymmetric.

2. NaCl-Type to NiO-Type. A number of years ago some powder diffraction studies utilizing a high-resolution technique[12-14] showed the occurrence of a second-order symmetry-breaking transition in NiO, FeO, and MnO. The low-symmetry structure has a rhombohedral lattice with no loss in translational symmetry (Figure 9), and thus the transition corresponds to $\vec{k} = 0$. In this case the irreducible representations are isomorphous with those of the point-group O_h. The irreducible representations yielding rhombohedral symmetry are then the triply degenerate T representations. The T_g representations yield third-order invariants, and the T_u representations do not, and it is concluded[9] that second-order transitions to $R\bar{3}$ and $R\bar{3}m$ are not allowed, while transitions to $R3m$ and $R32$ can occur as second-order processes. A continuous distortion of the NaCl-type structure to yield $R32$ symmetry yields atoms in the fixed positions with $R\bar{3}m$ symmetry, and thus such a continuous process is not possible. It can thus be concluded that a second-order distortion of the NaCl-type structure at $\vec{k} = 0$ to yield a rhombohedral lattice must yield the space group $R3m$. This Landau theory result clarifies the observations by establishing the noncentrosymmetric nature of the product.

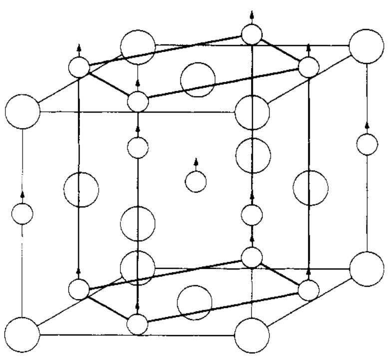

Figure 10. Tetragonal (*I4mm*) distorted structure proposed for CoO.

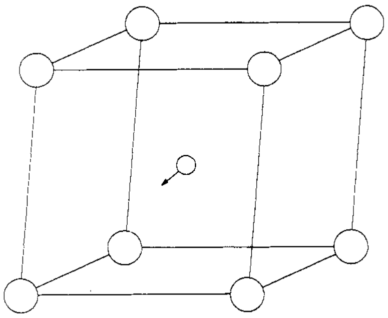

Figure 11. Rhombohedral (*R3m*) distorted structure proposed for LiPb.

3. NaCl-Type to CoO-Type. As in the monoxides of Ni, Fe, and Mn, CoO undergoes a second-order transition[14] without loss of translational symmetry. In this case the broken symmetry is tetragonal (Figure 10). This distortion corresponds to the same irreducible representation as does the rhombohedral distortion of section 2; however in this case the distorted structure has the symmetry of one of the functions of the triply degenerate set rather than of the sum of the three functions as in the rhombohedral case. This function is antisymmetric with respect to inversion, and thus Landau theory again yields a noncentrosymmetric space group, $I4mm$ in this case.

4. CsCl-Type to LiPb-Type. A distortion from CsCl-type to a rhombohedral lattice without loss of translational symmetry (Figure 11) has been reported to occur continuously in LiPb.[15] This distortion, as those

---

[12] Rooksby, H. P. *Acta Crystallogr.* **1948**, *1*, 226.

[13] Willis, B. T. M.; Rooksby, H. P. *Acta Crystallogr.* **1953**, *6*, 827.

[14] Tombs, N. C.; Rooksby, H. P. *Nature* **1950**, *165*, 442.

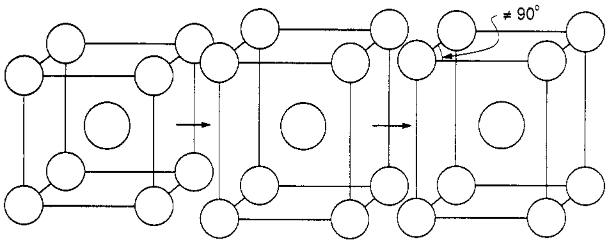

Figure 12. Cubic → tetragonal → orthorhombic ($Pm3m \rightarrow P4/mmm \rightarrow Cmmm$) transitions of RhTi, RuNb, and RuTa. The primitive monoclinic cell with $\gamma \neq 90°$ and $a = b$ is shown.

above, corresponds to the T_{2u} representation of O_h and is consistent with Landau theory only if the low-symmetry space group is noncentrosymmetric ($R3m$). The space group $R\bar{3}m$ was previously thought to be correct.[15]

5. Tetragonal to Orthorhombic Transition in VIr. Two structures for VIr with V/Ir = 1.17 have been reported. One is tetragonal with V predominantly at 0, 0, 0 and Ir predominantly at $^1/_2$, $^1/_2$, $^1/_2$ of the tetragonal cell (a = 2.770 Å, c = 3.651 Å, $P4/mmm$). The other is orthorhombic with $Cmmm$ symmetry and $a \cong 2a_{tet}$, $b \cong 2c_{tet}$ and $c \cong a_{tet}$. This distortion corresponds to $\vec{k} = {}^1/_2, 0, {}^1/_2$ (or $0, {}^1/_2, {}^1/_2$) and all of the symmetry operations of the $Cmmm$ subgroup of $P4/mmm$ carry $\vec{k} = {}^1/_2, 0, {}^1/_2$ into itself, i.e., the distortion corresponds to the totally symmetric "small" representation at $\vec{k} = {}^1/_2, 0, {}^1/_2$. This irreducible representation of the space group meets all the conditions of Landau theory. It follows that a second-order transition is allowed between the two VIr structures, and a high-temperature X-ray diffraction study[16] indicated that the transition does, in fact, occur continuously. It had been previously thought that the two structures were in one-phase regions separated by a two-phase region.[17]

6. Phase Transitions in RhTi. When RhTi with the CsCl-type structure is cooled from high temperatures, it transforms first to tetragonal symmetry via a first-order transition and then to orthorhombic symmetry via a second-order transition.[18] These transitions both occur without loss of translational symmetry (at $\vec{k} = 0$). The cubic to tetragonal transition appears to be to centrosymmetric $P4/mmm$, and as mentioned above such a transition is necessarily first order. The tetragonal to orthorhombic transition, on the other hand, apparently occurs as a second-order process. It has long been known[1,3] that a transition halving the number of symmetry operations necessarily meets the conditions of Landau theory. This is the case for $P4/mmm \rightarrow Cmmm$ at $\vec{k} = 0$, and thus the observed continuity of the process is consistent with Landau theory. This understanding clarifies previously confused[19] heterogeneous behavior in RhTi. Similar behavior has been observed for RuNb[20] and for RuTa,[21] in which the tetragonal-to-orthorhombic transition is first-order, however.

Conclusions

A variety of high-symmetry structures (NiAs-type, CsCl-type, NaCl-type, CuAu-type) undergo continuous symmetry breaking transitions with decreasing temperature. The nature of the broken symmetry is not always clearly discernible by using diffraction evidence. The Landau theory of symmetry and phase transitions provides theoretical guidelines that provide a strong basis for the determination of symmetry and structure in these cases.

Acknowledgment. The Ames Laboratory—DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

---

[15] Zalkin, A.; Ramsey, W. J. *J. Phys. Chem.* **1957**, *61*, 1413.

[16] Chen, B.; Franzen, H. F. *J. Less-Common Met.* **1990**, *195*, 343.

[17] Giessen, B. C.; Dangel, P. M.; Grant, N. J. *J. Less-Common Met.* **1967**, *13*, 62.

[18] Yi, S. S.; Chen, B.; Franzen, H. F. *J. Less-Common Met.* **1988**, *143*, 243.

[19] Kubaschewski-von Goldbeck, O. In *Atomic Energy Rev. Spec.*; Komarek, K. L., Ed.; Int. Atomic Energy Agency: Vienna, 1983; Issue 9.

[20] Chen, B.; Franzen, H. F. *J. Less-Common Met.* **1989**, *153*, L13.

[21] Chen, B.; Franzen, H. F. *J. Less-Common Met.* **1990**, *157*, 37.