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Symmetry Breaking Transitions in CsCl-Type Solids

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The Landau theory of symmetry and phase transitions is applied to the CsCl-type structure to determine the symmetry-allowed second-order phase transitions at the $\vec{k} = 0$ and $\vec{k} = (\vec{a}^* + \vec{b}^*)/2$ special points. Two distortions of CsCl-type that have been found experimentally, to the rhombohedral LiPb structure and to the orthorhombic AuCd-type structure, were found to meet the conditions of the theory. The AuCd-type was found to allow a further continuous distortion to the monoclinic NiTi structure that plays an important role in the shape memory of this material.

Introduction

A common feature of binary compounds of transition metals with high essential symmetries is the occurrence of symmetry breaking transitions with decreasing temperature. Numerous examples of this phenomenon have been reported for the NiAs-type structure (*1–3*), for the NaCl-type structure (*4–7*) and for the CsCl-type structure (*7–11*). In many of these cases the distortion corresponds to a single irreducible representation of the space group of the high-symmetry structure (*12, 13*). The interest in phase transitions of this general type has been greatly stimulated in recent years by the availability of a variety of techniques for band theoretical calculation of the energetic consequences of band splitting that results from the breaking of symmetry (*14, 15*).

Although the symmetry aspects of phase transitions in CsCl-type solids were investigated in some of the papers cited above, a complete treatment of the symmetry-breaking transitions possible for this structure type is not currently available. There are two known structures, LiPb and AuCd, which arise from apparently second-order phase transitions from the CsCl-type for which a symmetry analysis has not been reported. The purpose of this paper is to present a complete Landau theory analysis of the symmetry aspects of the phase transitions from CsCl-type to AuCd-type and to LiPb.

Application of Landau Theory

1. The LiPb Structure

The transition from CsCl-type to the rhombohedral LiPb structure was reported (*16*) to occur continuously. If the transition is second-order, as the observations suggest, then it must, by the Landau theory, correspond to a single irreducible representation. Because no superstructure results from the distortion the appropriate $\vec{k}$ point

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for the transition is $\vec{k} = 0$. At $\vec{k} = 0$ the small representations are isomorphous with the irreducible representations of the point group O_h. The one-dimensional irreducible representations all lead to cubic symmetries, and the two-dimensional irreducible representations lead to tetragonal or orthorhombic symmetries. The two three-dimensional irreducible representations which are symmetric with respect to inversion (T_{1g} and T_{2g}) yield third-order invariant combinations of basis functions, i.e., third-order terms in the Landau expansion for G, and thus cannot be active in a second-order transition. The remaining irreducible representations are those related to T_{1u} and T_{2u}.

The functions $\phi_1 = \sin 2\pi x$, $\phi_2 = \sin 2\pi y$, $\phi_3 = \sin 2\pi z$ transform as the T_{2u} related irreducible representations. No third-order invariant combinations of these functions can be constructed, and the general fourth-order invariant is

$$\sum_i \phi_i^4 + \lambda \sum_{i \neq j} \phi_i^2 \phi_j^2,$$

where λ is arbitrary. It follows that ΔG for the transition is, to fourth order, of the form

$$\Delta G = A\eta^2 + \left[C_1 \sum_{i=1}^{3} \gamma_i^4 + C_2 \sum_{i \neq j} \gamma_i^2 \gamma_j^2 \right] \eta^4,$$

which yields the thermodynamically stable solution when minimized subject to the restraint $\Sigma\gamma_i^2 = 1$. Two possible symmetries result, one has the symmetry of ϕ_1 (or ϕ_2 or ϕ_3), namely $P4mm$ with $a \cong c \cong a_{\text{cubic}}$, and the other has the symmetry of $\phi_1 + \phi_2 + \phi_3$, namely $R3m$ with $a \cong a_{\text{cubic}}$ and $\alpha \cong 90°$. The latter is consistent with the reported lattice for LiPb (*16*), but not with the suggested $R\bar{3}m$ symmetry. The T_{1u} case does not lead to an allowed distortion because the space group that corresponds to the $\phi_1 + \phi_2 + \phi_3$ solution, $R32$, would fix the positions of the atoms at 0,0,0 and 1/2,1/2,1/2, i.e., at the positions consistent with the $R\bar{3}m$ symmetry, which cannot result from a second-order phase transition because of the existence of a third-order invariant as discussed above (T_{1g}). The T_{2u}-related irreducible representation meets the fourth criterion of Landau theory, namely the antisymmetric square representation is orthogonal to the vector representation.

2. *The Distortion to AuCd-Type*

The transition from CsCl-type to AuCd-type (*Pmma* symmetry, $a \cong c \cong \sqrt{2}a_{\text{cubic}}$, $b \cong a_{\text{cubic}}$) has been observed in AuCd, AuTi, PdTi, and PtTi and apparently occurs as a second-order phase transition in these cases (*17*). The appropriate special point in this case is the M point ($\vec{k} = (\vec{a}^* + \vec{b}^*)/2$), and there are three wave vectors in the star. The small representations at this $\vec{k}$ point are isomorphous with the point group D_{4h}. The one-dimensional representations lead to space group symmetries in the D_{4h} crystal class, and thus these representations cannot be involved in the transition to AuCd-type. There are 2 two-dimensional irreducible representations of D_{4h}, and corresponding sets of basis functions in $Pm3m$ are given by

$$\phi_{1u} = \sin \pi x \cos \pi y$$

$$\phi_{2u} = \sin \pi y \cos \pi x$$

for the E_u case, and by

$$\phi_{1g} = \phi_{1u} \sin 2\pi z(\cos 2\pi x - \cos 2\pi y)(\cos 2\pi y - \cos 2\pi z)(\cos 2\pi z - \cos 2\pi x)$$

$$\phi_{2g} = \phi_{2u} \sin 2\pi z(\cos 2\pi x - \cos 2\pi y)(\cos 2\pi y - \cos 2\pi z)(\cos 2\pi z - \cos 2\pi x)$$

for the E_g case. For both E_g and E_u cases there are not third-order invariants and the minimization of G yields stable solutions for the particle density function, $\rho = \rho° + \phi_1\eta$ and $\rho = \rho° + (\phi_1 + \phi_2)\eta/\sqrt{2}$, where ϕ_1 and ϕ_2 are particle density functions with the appropriate symmetry. Examination of the functions yields the space group symmetries $Cmma$ ($a \cong b \cong 2a_{\text{cubic}}$, $c \cong a_{\text{cubic}}$) and $Pmna$ ($b \cong a_{\text{cubic}}$, $b \cong c \cong \sqrt{2}a_{\text{cubic}}$) for E_g, and $Cmmm$ ($a \cong b \cong 2a_{\text{cubic}}$, $c \cong a_{\text{cubic}}$) and

Pmma ($a \cong c \cong \sqrt{2}a_{\text{cubic}}$ and $b \cong a_{\text{cubic}}$) for E_u. The symmetry and cell of the $\phi_1 + \phi_2$ solution in the E_u case are those appropriate to the AuCd-type distortion of CsCl-type. A check of the fourth condition, as above, showed that this transition obeys this condition.

3. Distortion to $P2_1/m$ in AuCd-Type, the NiTi Structure

The structure of NiTi has been reported to have $P2_1/m$ space group symmetry with $a = 2.885$ Å, $b = 4.622$ Å, $c = 4.120$ Å, and $\beta = 96.8°$ (*18*). This structure suggests a distortion from the AuCd-type at the $\vec{k} = 0$ point. The corresponding small representations are isomorphous with the 8 one-dimensional representations of the D_{2h} point group, and each of these (except the totally symmetric) corresponds to halving the number of symmetry elements of *Pmma* and thus to an allowed second-order transition (*19*). Thus, three monoclinic distortions could result, $P2_1/m$ with the orthorhombic a axis becoming the unique axis, $P2/m$ with the orthorhombic b axis becoming the unique axis, and $P2_1/c$ with the orthorhombic c axis becoming the unique axis. The $P2_1/m$ alternative is consistent with the structure reported for NiTi.

Conclusions

The structures LiPb and AuCd-type are consistent with second-order formation from CsCl-type according to Landau's theory of symmetry and phase transitions (*19*). The NiTi structure is consistent with second-order formation from the AuCd-type.

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