Comment on "Irrelevant variables, Landau expansions, and cubic anisotropy"

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The relationship of the XY model, which arises from a C_{4v} image, to the phase transition in the rare-earth molybdate $Tb_2(MoO_4)_3$ (TMO) is discussed. We point out that this model does not describe the TMO transition, but that a Landau expansion arising from a C_4 image is the appropriate free-energy model.

Recently, Galam[1] considered phase transitions occurring in the XY model with cubic anisotropy. He emphasized, in a quite thorough discussion, that the extension of the Landau expansion to higher orders may significantly affect the resulting phase diagram. For the XY model, ϕ^8 terms generate a new symmetry breaking and the generic phase appears as a possible lower-symmetry phase.[1] Here we use the term "generic phase" to characterize the phase which has maximum symmetry breaking, i.e., the symmetry group mapped onto the identity matrix by the homomorphism. Higher-order terms beyond those of eighth order are "irrelevant" in that they do not introduce additional phase symmetries.

Within the Landau theory of phase transitions the free-energy expansion is constructed as an invariant function of the representation basis. It is usually assumed that the transition is driven by a single, multicomponent order parameter —the vector of an irreducible representation (irrep). The cubic XY model occurs in the description of many crystal systems (see Ref. 2 for an example of the XY model in surface transitions). It is defined by the representation of a space group whose complete set of distinct representation matrices (image) is isomorphic to the point group in two dimensions C_{4v}. Thus the set of symmetry transformations of the crystal map homomorphically onto a set of two-dimensional representation matrices equivalent to the usual vector representation of C_{4v}, namely, $\sigma_y = \left(\begin{smallmatrix}1 & 0\\ 0 & -1\end{smallmatrix}\right)$, $C_{4z}^- = \left(\begin{smallmatrix}0 & 1\\ -1 & 0\end{smallmatrix}\right)$, etc. The Landau expansion for the C_{4v} image is then an invariant polynomial expansion in terms of the order-parameter components. For C_{4v} the expansion can be constructed[3] as a polynomial expansion of the two basic invariants $I_1 = r^2$ and $I_2 = r^4\cos(4\theta)$. To eighth degree the free energy takes the form

$$F = \sum_{\alpha=1}^{4} u_\alpha I_1^\alpha + v_1 I_2 + w_1 I_1 I_2 + y_1 I_1^2 I_2 + y_2 I_2^2 \quad . \tag{1}$$

Here the terms with coefficients v_1, w_1, and y_i are anisotropic terms of fourth, sixth, and eighth degree, respectively. This form is equivalent to that used by Galam[1] and defines the XY model. As mentioned, the XY model is the polynomial expansion which is invariant under the order-parameter symmetry (image group) C_{4v}.

The C_{4v} image allows[3] *three* inequivalent lower-symmetry image subgroups, namely, $m(y)$, $m(d)$, and $\mathbf{1}$. Each image subgroup is the largest set of matrices leaving an order-parameter direction fixed. The subgroup $m(y)$ is the mirror subgroup (C_{1h}) with the mirror plane, $\sigma(y)$, defined by $\phi_2 = 0$. $m(d)$ has the mirror plane defined by $\phi_1 = \phi_2 \neq 0$. The image subgroup $\mathbf{1}$ is the subgroup corresponding to the identity transformation (identity matrix) in the two-dimensional representation space. Corresponding to each image subgroup a lower-symmetry crystalline phase (space group) is obtained as a result of the inverse of the homomorphic mapping. Thus there are three phases obtainable as minima of the expansion obtained from C_{4v}, or the cubic XY model. Only the subgroups obtained from $m(y)$ and $m(d)$ are possible when a fourth-order free-energy expansion is used (i.e., possible as continuous transitions) while all three are possible at eighth order and higher (possible as first-order transitions).[2,4] This is consistent with the major emphasis of Galam's paper.

However, Galam then incorrectly associates the cubic XY model with the first-order phase transition in terbium molybbate (TMO), $Tb_2(MoO_4)_3$. TMO is one of several rare-earth molybdates which has been well studied[5–7] and has many unusual properties. There is substantial structural evidence[6] that the transition in TMO is from a high-symmetry phase D_{2d}^3 to a lower-symmetry phase C_{2v}^8. For the space group D_{2d}^3 there are four images[8] (or irreps) which give the XY model. They are Γ_5, M_5, A_5, and Z_5 (we are using the labeling of Ref. 9). If a Hamiltonian of arbitrary degree (i.e., not just the fourth-degree expansion) is used, then the following phases can be obtained as inverses to $m(y)$, $m(d)$, and $\mathbf{1}$ and as minima of Eq. (1):

$$\Gamma_5(C_{1h}^3, C_2^2, C_1^1);\quad M_5(S_4^1, C_{2v}^4, C_2^1)\quad ;$$

$$A_5(S_4^2, C_{2v}^{22}, C_2^3);\quad Z_5(C_{2v}^{12}, D_2^4, C_2^2)\quad .$$

Notice that C_{2v}^8 is not possible as a minimum, at any order, of an XY model arising from irreps of D_{2d}^3. Thus the C_{4v} image (XY model) does not allow the known space-group changes in the transition of TMO and is not the appropriate model for its description. However, as we discuss below, there is a closely related image which does allow the space-group (and cell size) change for the transition.

The irreducible representation whose image is C_4 appears for several irreps of D_{2d}^3. The set of matrices are isomorphic to the point group (in two dimensions) C_4 and form a subgroup of C_{4v}. As one might expect, we obtain a larger number of basic invariants from C_4 than allowed in C_{4v}. The appropriate invariant free energy is constructed from the *three* invariants[3,5] $I_1 = r^2$, $I_2 = r^4\cos(4\theta)$, and $I_3 = r^4\sin(4\theta)$. To sixth degree the C_4 image yields the invariant free energy

$$F = \sum_{\alpha=1}^{5} u_\alpha I_1^\alpha + v_1 I_2 + v_2 I_3 + w_1 I_1 I_2 + w_2 I_1 I_3 \quad . \tag{2}$$

Notice that additional fourth-degree and sixth-degree terms are allowed with C_4 while not allowed with C_{4v}. The C_4 image occurs in particular for the $M_1 \oplus M_2$ irrep.[8] Moreover, this is the *only* irrep of D_{2d}^3 which can lead to C_{2v}^8 by means of an invariant free-energy expansion of a single order parameter. The image for this irrep, and thus the set of transformation matrices, will determine the corresponding Landau invariant expansion. This is compatible with the cell change and description in Ref. 5. The model obtained from the C_4 image is then the appropriate model for the description of TMO. The justification for a C_4 image depends only upon the observed space-group change from D_{2d}^3 to C_{2v}^8. From our list of possible subgroups[8] there is only one possible image subgroup arising from $M_1 \oplus M_2$ and it corresponds to the subgroup **1** of C_4 (while there are three subgroups for the C_{4v} image). This is consistent with the results of Gufan and Sakhnenko[3] for the C_4 image. The transition must always be to the generic phase, obtained as the inverse of **1** which is C_{2v}^8 for this case.

As can be seen from comparing the two models the two expansions are closely related. For example, the C_{4v} expansion can be obtained from the C_4 expansion by requiring $v_2(P,T)=w_2(P,T)=0$. It appears as though the C_{4v} model is obtained as a special case of the C_4 model. Also Ref. 6 indicates that by a choice of basis the v_2 and w_2 terms can be removed. We make the following arguments, however, to show that the models are not equivalent. First, the models are to describe regions of P, T space near the transition. The conditions $v_2(P,T)=w_2(P,T)=0$ can be satisfied for a point in the P-T plane but not in a region. Thus the additional fourth- and sixth-order terms in the C_4 free energy will appear for a dense set of P-T points. Similar arguments apply to the choice of basis at points in the P-T plane. Second, it is important to note that there is the significant difference in the order-parameter symmetries giving rise to the two free-energy expansions. The transformation properties of the C_{4v} order parameter are defined by the larger set of transformation matrices (larger image group). For example, the mirror reflection σ_y is not a transformation element of C_4 but it is an element of C_{4v}. When considering lower-symmetry phases we consider the largest set of transformations which leave an order-parameter direction fixed. For C_{4v}, this subgroup can contain σ_y. The element σ_y is not contained in the C_4 image. Thus the listing of subgroups for the C_{4v} image is different from the listing for the C_4 image. For C_4 only one subgroup is possible, while three are possible in C_{4v}.

Minimization of F in Eq. (2) is obtained from $\partial F/\partial r=0$, $\partial F/\partial\theta=0$, and the second derivative stability conditions. The condition $\partial F/\partial\theta=0$ leads to[6]

$$\tan(4\theta)=\frac{v_2+w_2r^2}{v_1+w_1r^2} . \quad (3)$$

Notice that if we restrict our attention to a continuous transition, and thus consider the free-energy expansion to fourth order, a continuous transition occurs at $u_1=0$, with

$$u_2+v_1\cos(4\theta)+v_2\sin(4\theta)>0 ,$$

and

$$\tan(4\theta)=\frac{v_2}{v_1} . \quad (4)$$

A continuous transition to the generic phase can occur along a line in pressure, temperature (P,T) variables for parameters restricted as above since we have the single equation $u_1(P,T)=0$. In distinction, the C_{4v} image does not allow a continuous transition to the generic phase even at a point in P,T variables. *Thus C_4 allows the possibility of a multicritical point appearing in* TMO *for the transition to the generic lower-symmetry phase.* As suggested by Bastie and Bornarel,[7] it would be interesting to apply hydrostatic pressure to a TMO crystal and determine if the system moves toward a tricritical point.

The transition for a C_4 image is distinctive in that the direction of the order parameter, determined by θ, can be temperature dependent near the tricritical (or multicritical) point. Considering only structural transitions, there are several solids in which a multicritical point is known to exist [(e.g., $BaTiO_3$ (Ref. 10), SbSI (Ref. 11), NH_4Cl (Ref. 12), and potassium dihydrogen phosphate (Ref. 13)]. Because of their image structures all are connected with transitions to a fixed order-parameter direction on the first-order side of (but near) the tricritical point even if the coefficients in the Landau expansion are assumed pressure and temperature dependent. For the free energy of Eq. (2) at a continuous transition, Eq. (4) implies no temperature dependence of θ when v_1 and v_2 are temperature independent. However, if the system is near a tricritical point on the first-order side (so that we need the expansion to sixth order for stability), then Eq. (3) implies a temperature dependence of θ even when v_1, v_2, w_1, and w_2 are independent of temperature. This temperature dependence comes from the order parameter r which varies as $(T-T_0)^{1/2}$ on the low-symmetry side of the transition.

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