an ion rate-limiting current. Hence a direct experimental measurement of the built-in potential together with its dependence on temperature and film thickness would be of the greatest value in establishing the domain of validity of the present model for any given system.

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SIMPLIFIED THEORY OF SYMMETRY CHANGE IN SECOND-ORDER PHASE TRANSITIONS: APPLICATION TO V_3Si †

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We report a simplification of the Landau theory, permitting more direct prediction of compatible space groups in second-order phase transitions. The theory is applied to the V_3Si transition, to predict that the lower symmetry space group is either $C_{4v}{}^7$-$P4mc$ or $D_{2d}{}^5$-$P\bar{4}m2$. The former possibility admits a polar axis.

In this Letter we report on a simplification of the thermodynamic (Landau) theory of second-order phase transitions[1] which permits the analysis to be carried out in a far more straightforward fashion than heretofore possible. The analysis will be applied to a case of a second-order phase transition in which there is much current interest: V_3Si; and some concrete predictions regarding the lower symmetry space group will be made, apparently for the first time.

Landau's theory has been presented in many

places,[2-4] so we only need to give a sufficiently complete description of it to make our simplification clear. The problem to be analyzed is the following: Given a crystal with space-group symmetry $\mathfrak{G}_0$ in the higher-symmetry phase, find all compatible space groups $\mathfrak{G}_1$, $\mathfrak{G}_1'$, $\mathfrak{G}_1''$, $\cdots$, in the sense that the latter can be achieved by second-order phase transition from the former. A necessary condition for compatibility is

$$\mathfrak{G}_1 \text{ is a subgroup of } \mathfrak{G}_0. \qquad \text{(A)}$$

To find sufficient conditions, an indirect approach is needed. Consider the atomic probability distribution, or density function, $\rho(\vec{r})$. The crystal symmetry group $\mathfrak{G}$ is the set of space-group operators $\{\vec{\varphi}\,|\,\vec{t}\}$ which leave $\rho(\vec{r})$ invariant. For $\rho(\vec{r})$ we write

$$\rho(\vec{r}) = \rho^{(0)}(\vec{r}) + \rho^{(1)}(\vec{r}), \qquad (1)$$

where $\rho^{(0)}(\vec{r})$ is invariant under all operations in $\mathfrak{G}_0$, and

$$\rho^{(1)}(\vec{r}) = \sum_{\sigma,m} c_\alpha^{(k_\sigma)(m)} \psi_\alpha^{(k_\sigma)(m)}(\vec{r}). \qquad (2)$$

In (2) $\rho^{(1)}$ is a linear functional of the basis vectors $\psi_\alpha^{(k_\sigma)(m)}$ of a single space-group irreducible representation $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$. These basis vectors may alternatively be defined[2] as the $c_\alpha^{(k_\sigma)(m)}$, which depend upon T and P. The Gibbs function of the crystal, Φ, is taken as a functional of the set $\{c_\alpha^{(k_\sigma)(m)}\}$ and expanded as

$$\Phi(\{c_\alpha^{(k_\sigma)(m)}\}) = \Phi^{(0)} + \Phi^{(1)} + \cdots + \Phi^{(s)} + \cdots, \qquad (3)$$

where $\Phi^{(s)}$ is a scalar homogeneous symmetric polynomial of sth degree in the $\{c_\alpha^{(k_\sigma)(m)}\}$. At any (T, P) the nonvanishing $\{c_\alpha^{(k_\sigma)(m)}\}$ are found by minimizing Φ; an evident physical constraint is that $\Phi_{\min}$ for $(T, P) > (T_c P_c)$ should correspond to all $c_\alpha^{(k_\sigma)(m)} = 0$ so that above the transition $\rho = \rho^{(0)}$, and the symmetry group of the crystal is $\mathfrak{G}_0$. But this constraint requires that for $(T, P) > (T_c P_c)$, $\Phi^{(1)} = \Phi^{(3)} = 0$. Since $\Phi^{(1)}$ vanishes in any event, an essential condition is $\Phi^{(3)} = 0$ by symmetry, or, in terms of space-group reduction coefficients,[5]

$$([\vec{\star}\vec{k}m]_{(3)}\,|\,\Gamma 1+) = 0, \qquad \text{(B)}$$

i.e., the symmetrized cube of $D^{(\vec{\star}\vec{k})(m)}$ shall not contain the identity representation $D^{(\Gamma)(1+)}$ of $\mathfrak{G}_0$. Spatial homogeneity imposes the requirement that the antisymmetrized square of $D^{(\vec{\star}\vec{k})(m)}$ shall not contain the representation of a polar vector $D^{(\Gamma)(v)}$, or

$$([\vec{\star}\vec{k}m]_{[2]}\,|\,\Gamma v) = 0. \qquad \text{(C)}$$

An acceptable irreducible representation of $\mathfrak{G}_0$ satisfies (B) and (C) and may be used in the construction of Φ, its minimization, and the subsequent determination of possible sets $\{c_\alpha^{(k_\sigma)(m)}\}$ and then the corresponding $\rho^{(1)}(\vec{r})$ and $\mathfrak{G}_1$. As previously formulated, and applied, each $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ must be separately tested for acceptibility and then used to find $\mathfrak{G}_1$; this is a lengthy[3] and, as shown below, an unnecessary process.

Our simplification is based upon an observation, working in the inverse order. If $\mathfrak{G}_1$ is a group compatible with $\mathfrak{G}_0$ then $\rho^{(1)}(\vec{r})$ is an invariant space for all $\{\vec{\varphi}_1\,|\,\vec{t}_1\}$ in $\mathfrak{G}_1$. But by construction, $\rho^{(1)}(\vec{r})$ is a space built from a complete set of basis vectors which produce $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$. But this set can produce an invariant space under $\mathfrak{G}_1$ if and only if

$$D^{(\vec{\star}\vec{k})(m)} \text{ of } \mathfrak{G}_0 \text{ subduces } D^{(\Gamma)(1+)} \text{ of } \mathfrak{G}_1. \qquad \text{(D)}$$

That criterion (D) gives <u>all</u> possible acceptable $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ is seen from the converse argument. An acceptable $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ can also be considered as induced from $D^{(\Gamma)(1+)}$ of $\mathfrak{G}_1$. By the Frobenius reciprocity theorem,[6] there will appear in the induced representation only those $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ which already satisfy (D). Of course, $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ may subduce other representations in $\mathfrak{G}_1$ in addition to $D^{(\Gamma)(1+)}$. Finally, if an acceptable $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ is one-dimensional, or if an acceptable $D^{(\vec{\star}\vec{k})(m)}$ of $\mathfrak{G}_0$ subduces only a multiple of $D^{(\Gamma)(1+)}$ of $\mathfrak{G}_1$ and no other representation, then $\mathfrak{G}_1$ is a normal subgroup of $\mathfrak{G}_0$. These simplifications permit one to work directly with the groups $\mathfrak{G}_0$ and $\mathfrak{G}_1$ and avoid the minimization of Φ required in the usual analysis.[3] Condition (D) is rigorously contained in the Landau theory, although stated explicitly here for the first time, we believe.

To conditions (A)-(D) it is plausible to add the rule

$$D^{(\vec{\star}\vec{k})(m)} \text{ of } \mathfrak{G}_0 \text{ corresponds to a physical tensor field.} \qquad \text{(E)}$$

Clearly (E) is not in the Landau theory but is implicitly used in most physical arguments. The field may be the normal coordinates $\vec{Q}(j\vec{k})$, macroscopic strain tensor $[\sigma]$, etc.

These considerations may now be applied to predict the space-group symmetry of the phase of V_3Si below the transition point[7] $T_m = 20.5°K$. This space group is presently not known. For $T > T_m$, V_3Si has symmetry $\mathfrak{G}_0 = O_h{}^3(Pm3n)$; at $T = T_m$ a second-order phase change occurs to a tetragonal structure, with the same unit cell, and with $c/a \simeq 1.0022$.

From (A), the only possible tetragonal space groups[8] are

$$D_{4h}{}^9(P4/mmc),\quad D_4{}^5(P4_22),\quad D_{2d}{}^2(P\bar{4}2c),$$
$$C_{4v}{}^7(P4mc),\quad \text{and}\quad D_{2d}{}^5(P\bar{4}m2). \tag{4}$$

Since the unit cell is unchanged, an acceptable $D^{(\bigstar\vec{k})(m)}$ of $\mathfrak{G}_0$ must have $\bigstar\vec{k} = \Gamma$, to be used in $\rho^{(1)}(\vec{r})$. Thus we need only concern ourselves with the ten irreducible representations of $O_h{}^3/\mathfrak{T}$, i.e., of O_h. Similarly the irreducible representation $D^{(\Gamma)(1+)}$ of $\mathfrak{G}_1$ only requires consideration of the point groups isomorphic to $\mathfrak{G}_1/\mathfrak{T}$. Using the subduction criterion (D) we obtain Table I which gives possible acceptable irreducible representations[9] of $\mathfrak{G}_0$ for each $\mathfrak{G}_1$. Using criteria (B) we find

$$A_{1g},\quad E_g,\quad F_{2g} \tag{5}$$

not acceptable. Criterion (C) gives nothing beyond (5). {Parenthetically we observe that the representations (5) are those by which the strain tensor $[\sigma]$ transforms, so $[\sigma]$ is not an acceptable physical tensor field.[10]} Application of (5) eliminates $D_{4h}{}^9$. This follows directly from the conditions (A)-(D) only.

Table I. Possible acceptable representations.[a]

$\Gamma^{(m)}$ of $O_h = \mathfrak{G}_0/\mathfrak{T}$	$\Gamma^{(m)}$ of $\mathfrak{G}_1/\mathfrak{T}$
A_{1g}; E_g	A_{1g} of $D_{4h}{}^9$
A_{1g}; E_g; A_{1u}; E_u	A_1 of $D_h{}^5$
A_{1g}; E_g; F_{1u}	A_1 of $C_{4v}{}^7$
A_{1g}; E_g; A_{2u}; E_u	A_1 of $D_{2d}{}^2$
A_{1g}; E_g; F_{2u}	A_1 of $D_{2d}{}^5$

[a]E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc., New York, 1955).

Now we use (E) and take the physical field to be the optic-mode normal coordinates in V_3Si at $\bigstar\vec{k} = \Gamma$, which are

optic modes:

$$A_{2g} \oplus E_g \oplus F_{1g} \oplus 2F_{1u} \oplus F_{2g} \oplus 2F_{2u}. \tag{6}$$

From (5) and (6) and the left-hand side of Table I we see that only modes F_{1u} and F_{2u} are acceptable. As there are no modes in (6) of symmetry A_{1u} or E_u, space group $D_4{}^5$ is eliminated.

Each of the three remaining possible groups has at least one "free" internal structure parameter to be specified in addition to c/a. We take each such parameter to represent a Cartesian component of an atom displacement from its corresponding position in $\mathfrak{G}_0$ (in which the parameter vanishes and $c/a = 1$). The resulting pattern of displacements in each case is then analyzed into normal modes of $\mathfrak{G}_0$. We

Table II. Predicted lower symmetry space groups.[a]

Site	Symmetry	Coordinates	Atom
		$\mathfrak{G}_1$: $C_{4v}{}^7(P4mc)$	
(c)	C_{2v}	(0,1/2,1/2+u), (1/2,0,u)	Si
(a)	C_{2v}	(0,0,1/4+v), (0,0,3/4+v)	V
(e)	C_s	(1/4,1/2,w), (1/2,1/4,1/2+w)	V
		(3/4,1/2,w), (1/2,3/4,1/2+w)	
		$\mathfrak{G}_1$: $D_{2d}{}^5(P\bar{4}m2)$	
(g)	C_{2v}	(0,1/2,1/4+p), (1/2,0,3/4−p)	Si
(a)	D_{2d}	(0 0 0)	V
(d)	D_{2d}	(0,0,1/2)	V
(k)	C_s	(1/4,1/2,3/4+q), (1/2,1/4,1/4−q)	V
		(3/4,1/2,3/4+q), (1/2,3/4,1/4−q)	

[a]"Symmetry Groups," in International Tables for X-Ray Crystallography, edited by N. F. M. Henry and K. Lonsdale (Kynoch Press, Burmingham, England, 1952), Vol. 1.

find that for the transition $O_h^3 \rightarrow D_{2d}^2$, modes of symmetry E_g are required. This violates (5) and eliminates D_{2d}^2. To go from $O_h^3 \rightarrow C_{4v}^7$ requires modes of symmetry $F_{1u} \oplus E_g$. To go from $O_h^3 \rightarrow D_{2d}^5$ requires $F_{2u} \oplus E_g$. But by assumption, only one acceptable irreducible representation may occur in (2). This obliges us to take certain parameters as zero in C_{4v}^7 and D_{2d}^5, so that E_g does not occur in the displacement pattern. The result of this analysis and hence the predicted compatible subgroups C_{4v}^7 and D_{2d}^5 are given in Table II. The atom positions and site symmetry is given with the minimum number of free parameters in each case. Observe that one possibility, C_{4v}^7, possesses a polar axis, which would permit ferroelectricity, as recently speculated.[10] The different site symmetry of certain V atoms in the two cases may permit an indirect structure determination, although recent work could not resolve such possibilities.[11]

Recently[12] another mechanism for the transitions has been proposed, based on an electron-lattice interaction, in which the V atom distortions (along the chain) had symmetry E_g. In that work, it was necessary to identify the transition as first order, in contradiction to other workers, and to the analysis presented here, since E_g is not acceptable. Determination of the lower symmetry structure should resolve this conflict.

The writer believes that the simplification presented here will enable much more use to be made of the Landau theory so that the "dichotomous"[13] symmetry predictions of the theory can be examined apart from the theory's analytical predictions. The latter are known to be inapplicable in cases where the symmetry argument apparently holds.

Note added in proof.—After this Letter was submitted, the writer learned of some independent work by Professor R. Loudon (private communication) on the same subject. Loudon's analysis was based on point-group considerations; his conclusions regarding point-group symmetry of the low-temperature phase agree with those presented here. He did not, however, predict possible full space-group symmetry of the low-temperature phase.

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