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Acoustic phonon instabilities and structural phase transitions

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Structural phase transitions are considered in which the order parameter is a homogeneous deformation of the crystal. The fluctuations at these transitions are the acoustic modes, and it is shown that an effective Hamiltonian may be constructed describing the homogeneous deformations and their fluctuations. There are three cases which result, those in which there are no fluctuations with wavelengths less than the crystal dimensions, those in which the acoustic modes have strongly temperature-dependent velocities for wave vectors on particular lines of reciprocal space, and those for which the velocities are temperature dependent for wave vectors within planes in reciprocal space. In many cases, the transitions are expected to be first order because of the presence of cubic invariants in the effective Hamiltonian. In those which may be continuous, the behavior is shown by use of renormalization-group theory to be that of classical Landau theory, with the possibility of logarithmic corrections in one particular instance. Unfortunately, we are unaware of any examples of this case, but in the other cases, the results are in accord with experimental results.

I. INTRODUCTION

During the last few years, considerable progress has been made in the understanding of the effects of fluctuations on critical phenomena. The renormalization-group technique[1] has enabled the Landau theory of phase transitions to be extended to take account of fluctuations at least approximately, and has provided justification for the universality hypothesis for critical phenomena; namely, that systems having the same symmetry are expected to have similar critical properties. The application of these ideas to structural phase transitions has provided considerable insight, but has also shown that there can be a wide variety of behavior at different phase transitions dependent upon the number of components of the ordering variable, the dimensionality of the system, and the symmetry of the interactions.

In this paper, we consider structural phase transitions at which a homogeneous deformation of the unit cell of the crystal is the primary order parameter. At most, if not all, structural phase transitions there is a small deformation of the unit cell, but this is most frequently because the homogeneous strain parameter is a secondary order parameter. For example, in the ferroelectric phase transition of $BaTiO_3$, the ferroelectric displacements are the primary order parameter and these are coupled to the tetragonal strain parameters by a term which is linear in the strain and quadratic in the ferroelectric displacements. This is an example of a compressible ferroelectric phase transition. In the type of phase transition considered in this paper, the homogeneous strain is a primary order parameter and we expect in at least some cases that some combination of the elastic constants will become small above T_c. Examples of this type of phase transition[2] are the structural phase transition in Nb_3Sn, the ferroelectric phase transition in KH_2PO_4, and the phase transition in $DyVO_4$. In each of these cases, there is a different origin for the temperature dependence of the elastic constant: electronic band structure, ferroelectric fluctuations, or the Jahn-Teller effect, but these effects have the same symmetry as the appropriate homogeneous deformation.

The stability of crystals against homogeneous deformations is discussed in the text by Born and Huang[3] using macroscopic elasticity theory. It is not difficult to construct a Landau expansion for the free energy in a power series in these strain parameters. In order to go beyond Landau theory it is necessary to include the fluctuations. Frequently extending a Landau expansion to include fluctuations is straightforward, but in this case there is considerably more difficulty. The difficulty arises because the fluctuations are long-wavelength acoustic waves in the crystal and are normally described by lattice dynamics instead of macroscopic elasticity theory. A large part of Sec. II discusses this difficulty and shows how it may be overcome and may lead to different types of behavior. The different possible types of phase transition which may occur are then classified for all of the different crystal classes.

In Sec. III these results are used to construct effective Hamiltonians for these phase transitions which are then analyzed using renormalization-group theory in Sec. IV. In Sec. V the results are discussed and the predictions compared with the available experimental results.

II. ELASTICITY THEORY AND ACOUSTIC WAVES

A. Stability conditions

A homogeneous deformation of a crystal is described by the components of the strain tensor $e_{\alpha\beta}$ in terms of which the displacement $\vec{u}(\vec{r})$ of an atom at $\vec{r}$ is given by

$$u_\alpha(\vec{r}) = \sum_\beta e_{\alpha\beta} r_\beta .$$

The strain energy density of the crystal can then be expressed in terms of these strain components and the isothermal elastic constants as

$$U = \frac{1}{2} \sum_{\alpha\beta\gamma\lambda} c_{\alpha\beta\gamma\lambda} e_{\alpha\beta} e_{\gamma\lambda} . \qquad (1)$$

Since the elastic constants are symmetric in the $\alpha\beta$ and $\gamma\lambda$ indices, it is frequently useful to rewrite this expression in the Voigt notation when

$$e_\rho = e_{\alpha\beta}, \quad \alpha=\beta=\rho ,$$

$$e_\rho = e_{\alpha\beta} + e_{\beta\alpha}, \quad \alpha \neq \beta, \quad \rho = 9 - \alpha - \beta .$$

In the Voigt notation the energy density is

$$U = \frac{1}{2} \sum_{\rho\sigma} c_{\rho\sigma} e_\rho e_\sigma , \qquad (2)$$

where $c_{\rho\sigma} = c_{\alpha\beta\gamma\lambda}$. Symmetry may then be used to reduce the number of independent elastic constants as described by Nye.[4]

The crystal is stable against homogeneous deformations if the elastic constant matrix $c_{\rho\sigma}$ has positive eigenvalues.[3] If one or more of the eigenvalues decreases to zero, the crystal may distort continuously to a new structure with a symmetry determined by the eigenvector of that eigenvalue. For example, in the case of a cubic crystal the elastic constant matrix has three eigenvalues: a singlet of symmetry A_1 associated with the eigenvalue $c_{11} + 2c_{12}$, a doublet E with eigenvalue $c_{11} - c_{12}$, and a triplet T_2 with eigenvalue c_{44}. The first of these eigenvectors corresponds to a change in the volume of the crystal, the second to an expansion along one cube axis and an equivalent contraction along another, and the third to a shear of the unit cell.

B. Acoustic waves

In the theory of phase transitions it is necessary to consider the effect of fluctuations in the order parameter with wave vectors close to, but different from, the wave vector of the ordering field. In the present case, the fluctuations of the strains with small wave vectors, $\vec{q}$, are acoustic waves and must be treated by the methods of lattice dynamics.[3] The displacements in an acoustic wave with wave vector $\vec{q}$ are given by

$$\vec{u}(\vec{r}) = \vec{w} e^{i\vec{q}\cdot\vec{r}}$$

and the strain generated by this wave is given by

$$e_{\alpha\beta} = \delta u_\alpha / \delta r_\beta = i q_\beta w_\alpha e^{i\vec{q}\cdot\vec{r}} . \qquad (3)$$

The equation of motion of elasticity theory is then

$$\rho \omega^2 w_\alpha = \sum_\beta M_{\alpha\beta}(\vec{q}) w_\beta ,$$

where ρ is the density of the crystal and

$$M_{\alpha\beta}(\vec{q}) = \sum_{\gamma\lambda} c_{\alpha\gamma\beta\lambda} q_\gamma q_\lambda .$$

For each wave vector $M_{\alpha\beta}(\vec{q})$ has three eigenvalues and eigenvectors corresponding to the three acoustic modes of vibration for each wave vector. In general these eigenvectors do not produce those combinations of the strains which are the eigenvectors of the elastic constant matrix, and furthermore the eigenvalues of this matrix are not the eigenvalues of the elastic constant matrix, but linear combinations of them. These complications arise in part because the elastic constant matrix $c_{\rho\sigma}$ is a 6×6 matrix whereas the $M_{\alpha\beta}(\vec{q})$ is only a 3×3 matrix.

This difficulty can be illustrated by the example of a cubic crystal. When the wave vector is along [100], the longitudinal mode is a linear combination of the strains $(1/\sqrt{3})A_1 + (\sqrt{2}/\sqrt{3})E$, with an elastic constant c_{11}. The transverse modes give pure T_2 strains with elastic constant c_{44}. When the wave vector is along the [110] direction the longitudinal mode gives a linear combination of the A, E, and T_2 strains, the transverse mode polarized along $[1\bar{1}0]$ gives a pure E strain and the transverse mode polarized along [001] a pure T_2 strain.

The energy density associated with the acoustic modes is a sum over all the wave vectors and over all three different branches. When this is rewritten in terms of the strains each acoustic wave will contribute to the energy density an amount proportional to the elastic constant of that wave and multiplied by the appropriate combination of eigenvectors dependent upon the acoustic wave.

Close to a phase transition associated with a homogeneous deformation one of the eigenvalues of the elastic constant matrix becomes small and the behavior will be dominated by the fluctuations of the lattice waves with the smallest velocities. The velocity of an acoustic wave is a linear combination of the elastic constants for the different irreducible representations of the elastic constant matrix. Except by chance, there will be only one of these irreducible representations for which the elastic constant becomes very small. It follows, therefore, that the velocity of the acoustic waves will become vanishingly small for only those waves for which the distortion is purely that of the irreducible representation of the elastic constant matrix with the smallest eigenvalue. In order to discuss the fluctuations at these phase transitions the behavior of the acoustic waves in the neighborhood of these special acoustic modes must be examined.

In a cubic crystal the expression for $M_{\alpha\beta}(\vec{q})$ is

$$M_{\alpha\beta}(\vec{q}) = (c_{12}+c_{44})q_\alpha q_\beta + [c_{44}\vec{q}^2 + (c_{11}-c_{12}-2c_{44})q_\alpha^2]\delta_{\alpha\beta}. \qquad (4)$$

If the smallest eigenvalue of the elastic constant matrix is c_{44} and the associated strains of T_2 symmetry, the acoustic waves with the smallest velocities are the transverse waves polarized along a cube axis and propagating perpendicular to that cube axis. The behavior of the velocities for wave vectors $\vec{q}=(q_x,q_y,q_z)$ can be obtained from Eq. (4). If q_z/q is small the smallest velocity is determined by the expression

$$c_{44} + \frac{c_{11}-c_{12}-2c_{44}}{c_{11}+c_{12}}(c_{11}+2c_{12}+c_{44})\frac{q_z^2}{q^2}. \qquad (5)$$

As $c_{44}\to 0$ the velocity of the acoustic waves decreases for all the modes propagating in the (xy) plane, but for modes propagating out of this plane the velocity does not become zero as $c_{44}\to 0$. In this case, for which the acoustic waves propagating in a plane have their velocities determined by the eigenvalues of the elastic constant matrix, the behavior will be denoted type II.

In the derivation of Eq. (5), c_{44} was assumed to be much less than $c_{11}-c_{12}$ or $c_{11}+2c_{12}$. The second term is therefore necessarily positive. If the material is elastically isotropic, $c_{11}-c_{12}-2c_{44}=0$, the velocity of the acoustic waves is independent of direction, type III behavior. For a crystalline material undergoing a phase transition this requires the unrealistic assumption that $c_{11}-c_{12}$ and $2c_{44}$ change by the same amounts with temperature. This case is therefore only applicable for amorphous materials.

If the smallest eigenvalue of the elastic constant matrix is $c_{11}-c_{12}$, the only acoustic modes whose velocities are determined by this eigenvalue are the waves propagating along [110] directions and transversely polarized along $[1\bar{1}0]$. If $q_\perp$ is the component of the wave vector along $[1\bar{1}0]$ and q_z the component along [001] while $q_\perp$ and q_z are small compared with q, the velocity of these waves in the neighborhood of the [110] direction is given by

$$\tfrac{1}{2}(c_{11}-c_{12}) + (c_{44}-\tfrac{1}{2}c_{11}+\tfrac{1}{2}c_{12})\left(\frac{q_z^2}{q^2}+\frac{c_{11}+c_{12}}{c_{12}+c_{44}}\frac{q_\perp^2}{q^2}\right). \qquad (6)$$

In this case, type I, the velocity of the waves is determined by the eigenvalue of the elastic constant only along the [110] lines. Since $c_{11}-c_{12}$ has been assumed to be the smallest eigenvalue the coefficients of q_z^2 and $q_\perp^2$ are both positive.

Finally, if the smallest eigenvalue of the elastic constant matrix is $c_{11}+2c_{12}$, there are no acoustic waves with a velocity determined solely by this eigenvalue. This may be verified by symmetry. The A_1 irreducible representation has the full cubic symmetry. The introduction of a wave vector of necessity breaks some symmetry elements so that an acoustic wave cannot have complete A_1 symmetry. This type of behavior is denoted type 0.

C. Different crystal classes

In Secs. II A and II B the conditions for the stability of crystals and the behavior of the acoustic modes was discussed with particular reference to cubic crystals. These considerations may be extended to all of the different crystal classes and the results are listed in Table I. For each crystal class, the irreducible representations of the elastic constant matrix are listed using the notation of Heine[5] and for the elastic constants of Nye.[4] The stability criteria are listed for each of the different irreducible representations by giving the elastic constant expressions which must be greater than zero for stability.

The behavior of the acoustic waves with velocities determined solely by the eigenvalues of the elastic constant matrix is also listed in the table. For type-I behavior the special directions of the wave vectors are given together with the polarization vectors of the acoustic modes, while for type-II behavior the directions perpendicular to the special planes of wave vectors are given.

The only examples which have not been discussed in Sec. II B are those which occur when the elastic constant matrix has two or more irreducible representations of the same symmetry. For example, the $2A_1$ representations in the hexagonal, or trigonal classes. In these cases, there is in general no acoustic wave whose velocity is zero when the elastic constant stability condition given in Table I is equal to zero. In special instances, if $c_{13}=0$ while $c_{33}\to 0$, for example, there is an acoustic mode whose velocity $\to 0$. In general, this is not the case and there is no requirement that an acoustic mode must have zero velocity when a stability condition is violated.

TABLE I. Homogeneous deformations, stability conditions, and acoustic waves.

Representation	Strain	Stability condition	Acoustic waves	Cubic invariant
Cubic classes				
A_1	$e_1=e_2=e_3$	$c_{11}+2c_{12}$	0	Yes
E	$e_1=-e_2$	$c_{11}-c_{12}$	I $\vec{q} \parallel [110]$	Yes
	$e_3=-2e_1=-2e_2$		$\vec{u} \parallel [1\bar{1}0]$	
T_2	e_4, e_5, e_6	c_{44}	II $q \perp [100]$	Yes
			$\vec{u} \parallel [100]$	
Hexagonal classes				
$2A_1$	$e_1=e_2; e_3$	$(c_{11}+c_{12})c_{33}-2c_{13}^2$	0	Yes
E_2	$e_1=-e_2, e_6$	$c_{11}-c_{12}$	II $\vec{q} \perp [001]$	Yes
			$\vec{u} \perp [001]$ and $\vec{q}$	
E_1	e_4, e_5	c_{44}	II $\vec{q} \perp [001]$	Yes
			$\vec{u} \parallel [001]$	
Trigonal classes 32, $\bar{3}m$, $3m$				
$2A_1$	$e_1=e_2; e_3$	$(c_{11}+c_{12})c_{33}-2c_{13}^2$	0	Yes
$2E$	$e_1=-e_2, e_4; e_5, e_6$	$(c_{11}-c_{12})c_{44}-2c_{14}^2$	0	Yes
Trigonal classes 3, $\bar{3}$				
$2A$	$e_1=e_2; e_3$	$(c_{11}+c_{12})c_{33}-2c_{13}^2$	0	Yes
$2E$	$e_1=-e_2, e_4; e_5, e_6$	$(c_{11}-c_{12})c_{44}-2c_{14}^2-2c_{15}^2$	0	Yes
Tetragonal classes $4mm$, $\bar{4}2m$, 422, $4/mmm$				
$2A_1$	$e_1=e_2; e_3$	$(c_{11}+c_{12})c_{33}-2c_{13}^2$	0	Yes
B_1	$e_1=-e_2$	$c_{11}-c_{12}$	I $\vec{q} \parallel [110]$	No
			$\vec{u} \parallel [1\bar{1}0]$	
B_2	e_6	c_{66}	I $\vec{q} \parallel [100]$	No
			$\vec{u} \parallel [010]$	
E	e_4, e_5	c_{44}	II $\vec{q} \perp [001]$	No
			$u \parallel [001]$	
Tetragonal classes 4, $\bar{4}$, $4/m$				
$2A$	$e_1=e_2; e_3$	$(c_{11}+c_{12})c_{33}-2c_{13}^2$	0	Yes
$2B$	$e_1=-e_2; e_6$	$(c_{11}-c_{12})c_{66}-2c_{16}^2$	0	No
E	e_4, e_5	c_{44}	II $\vec{q} \perp [001]$	No
			$\vec{u} \parallel [001]$	
Orthorhombic classes				
$3A_1$	$e_1; e_2; e_3$	K_1	0	Yes
B_1	e_6	c_{66}	I $\vec{q} \parallel [010]$ or $[100]$	No
			$\vec{u} \parallel [100]$ or $[010]$	
B_2	e_5	c_{55}	I $\vec{q} \parallel [100]$ or $[001]$	No
			$\vec{u} \parallel [001]$ or $[100]$	
B_3	e_4	c_{44}	I $\vec{q} \parallel [001]$ or $[010]$	No
			$\vec{u} \parallel [010]$ or $[001]$	
Monoclinic classes				
$4A$	$e_1; e_2; e_3; e_5$	K_2	0	Yes
$2B$	$e_4; e_6$	$c_{44}c_{66}-c_{46}^2$	0	No
Triclinic classes				
$6A$	$e_1; e_2; e_3; e_4; e_5; e_6$	K_3	0	No
Isotropic classes				
$L=0$	$e_1=e_2=e_3$	$3c_{12}+2c_{44}$	0	Yes
$L=2$	e_4, e_5, e_6	c_{44}	III $\vec{u} \perp \vec{q}$	Yes
	$e_1=-e_2$			
	$e_3=-2e_1=-2e_2$			

$K_1=\det|c_{ij}|,\quad i, j \le 3$
$K_2=\det|c_{ij}|,\quad i, j \le 3$ or 5
$K_3=\det|c_{ij}|,\quad i, j \le 6$

III. EFFECTIVE HAMILTONIAN

A. Landau expansion

In the Landau theory of phase transitions the free energy is expanded as a power series in the order parameter. In Sec. II A the form of the quadratic term was discussed for homogeneous deformations. In this section the form of the cubic and quartic terms in this expansion are described. If there is a cubic invariant of the order parameter then the Landau theory of phase transitions shows that the phase transition is of first order.[6] The presence of a third-order invariant is determined by the symmetry of the irreducible representation of the elastic constant matrix and the results are listed in Table I. Clearly, many phase transitions against homogeneous deformations are of first order. If the third-order invariant is sufficiently small at these transitions it may well be that the elastic constant becomes very small and the fluctuations very large before the transition occurs as indeed seems to be the case in Nb_3Sn.[7]

There are, however, nine cases shown in Table I for which the third-order invariants are absent by symmetry, and for which the transitions may be continuous provided that the quartic interactions are positive. In these cases, the form of the interactions may be obtained either from the fourth-order elastic constants or by symmetry.

In the cases where the irreducible representation of the elastic constant matrix is a singlet, the Landau free energy is given by

$$F_{\mathrm{I}} = V_2 e^2 + V_4 e^4 ,$$

where V_2 is the appropriate combination of elastic constants for the strain e, and V_4 is determined by the fourth-order elastic constants. When the irreducible representation is a doublet with components e_1 and e_2, the free energy is given by

$$F_{\mathrm{II}} = V_2(e_1^2+e_2^2) + V_4(e_1^2+e_2^2)^2 + W_4(e_1^4+e_2^4) . \tag{7}$$

A similar expression may be written down for the T_2 triplet modes in the cubic system.

B. Fluctuations

The Landau theory of phase transitions may be extended to include the effects of fluctuations by including the effects of strains with wave vectors $\vec{q}$ which are nonzero. If the irreducible representation of the elastic constant matrix is a singlet, a continuous phase transition may occur if there are no acoustic waves or if they are of type I, as shown in Table I. In the former case, fluctuations of the strain will occur only for wavelengths comparable with the crystal dimensions, and consequently deviations from Landau theory will only occur extremely close to T_c, except for very small crystals.

In the latter case, the acoustic waves are type I and their dependence upon q is described by Eq. (6). In the case of the B_2 representation of the tetragonal classes the term quadratic in the strain may be written approximately as

$$\frac{1}{2}\sum_{q} (c_{66} + \lambda_1 \cos^2\phi \sin^2\phi \sin^2\theta + \lambda_2 \cos^2\theta + Kq^2) e_6(\vec{q}) e_6(-\vec{q}) , \tag{8}$$

where the wave vector $\vec{q}$ has been written in spherical polar coordinates and λ_1 and λ_2 are the appropriate expressions of the elastic constants which yield the coefficients of $q_\perp^2/q^2$ and q_z^2/q^2. The term Kq^2 describes the dispersion of the acoustic waves. In general, this term should be anisotropic, but the anisotropy does not change the later results significantly. A similar result to Eq. (8) can be obtained for the B_1 representation except that c_{66} is replaced by $\frac{1}{2}(c_{11}-c_{12})$ and the origin of the ϕ angle is rotated by $\frac{1}{4}\pi$. Similarly, Eq. (8) is applicable for the orthorhombic class with a strain of B_1 symmetry, while the corresponding expressions for B_2 and B_3 symmetries may be obtained by appropriate interchange of axes.

The effective Hamiltonian may then be written in the notation usually adopted for calculations using renormalization-group theory by appropriate rescaling as

$$\mathcal{H} = -\frac{1}{2}\int_{\vec{q}} (r + g\cos^2\phi \sin^2\phi \sin^2\theta + h\cos^2\theta + q^2) S(\vec{q}) S(-\vec{q}) - u_0 \int_{\vec{q}_1}\int_{\vec{q}_2}\int_{\vec{q}_3} S(\vec{q}_1) S(\vec{q}_2) S(\vec{q}_3) S(-\vec{q}_1-\vec{q}_2-\vec{q}_3) , \tag{9}$$

where the coefficients g_1, g_2, and u_0 are given in terms of the elastic constants.

The effective Hamiltonian for the strains with E symmetry in the tetragonal classes is more complex because the representation is two dimensional. The acoustic waves are type I and, in general, correspond to a linear combination of the two basis representations determined by the direction of propagation in the (xy) plane. By using the analogy of this problem to that of dipolar systems[8] an effective Hamiltonian may be constructed as

$$\mathcal{H} = \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2} -\frac{1}{2}\int_{\vec{q}} U^2_{\alpha\beta}(\vec{q}) S_\alpha(\vec{q}) S_\beta(-\vec{q}) - (u_0 + \delta_{\alpha\beta} v_0) \int_{\vec{q}_1}\int_{\vec{q}_2}\int_{\vec{q}_3} S_\alpha(\vec{q}_1) S_\alpha(\vec{q}_2) S_\beta(\vec{q}_3) S_\beta(-\vec{q}_1-\vec{q}_2-\vec{q}_3) , \tag{10}$$

where

$$U^2_{\alpha\beta}(\vec{q}) = \left(r_0 + \vec{q}^2 + f_0 q_\alpha^2 + g_0 \frac{q_z^2}{\vec{q}^2}\right)\delta_{\alpha\beta} + h_0 \frac{q_\alpha q_\beta}{\vec{q}^2}$$

and the limit is taken as $h_0 \to \infty$.

In this expression terms of order q_z^2 and $q_\alpha q_\beta$ have been neglected as they do not significantly alter the results. If the system is isotropic in the (xy) plane the terms f_0 and v_0 are zero.

IV. PHASE TRANSITIONS

A. Singlet case

In this section standard renormalization-group theory[1] is used to elucidate the properties of the phase transitions described by the effective Hamiltonians obtained above. The Hamiltonian given in Eq. (9) is very similar to that of uniaxial dipolar systems discussed in detail by Aharony.[9] It may be treated in the same way to obtain the differential form of the recursion relations for the parameters g, h, and u, which to lowest order are

$$\frac{dg_l}{dl} = 2g_l, \quad \frac{dh_l}{dl} = 2h_l \tag{11}$$

and

$$\frac{du_l}{dl} = u_l - 36u_l^2 B(g_l, h_l), \tag{12}$$

where

$$B(x,y) = \int_0^{2\pi}\int_0^{\pi} \frac{\sin\theta\, d\theta\, d\phi}{(1 + x\cos^2\theta + y\sin^2\theta\cos^2\phi\sin^2\phi)^2}. \tag{13}$$

From Eqs. (11) $g_l = g_0 e^{2l}$ and $h_l = h_0 e^{2l}$ showing that g_l and $h_l \to \infty$ as $l \to \infty$. The integrals in Eq. (13) may be performed approximately if x and y are large to give

$$B(x,y) \approx \pi(xy)^{-1/2}.$$

The recursion relation for u_l then becomes for large l

$$\frac{du_l}{dl} = u_l - 36\pi u_l^2 (g_0 h_0)^{-1/2} e^{-2l},$$

which may be solved to obtain an expression for u_l which for large l is

$$u_l = \frac{e^l}{1/u_0 + 36\pi/(g_0 h_0)^{1/2}}.$$

Since u_l is increasing with l it is unclear that the expansions to lowest order in u_l are valid. As, however, in the dipolar problem[9] the expansion parameter is not u_l, but $u_l(g_l h_l)^{-1/2}$. In this case this parameter behaves like e^{-l} as $l \to \infty$. The power series is therefore rapidly convergent and Landau theory is expected to be valid. The borderline between classical and nonclassical behavior which is at $d=4$ for short-range systems[1] and $d=3$ for uniaxial dipolar systems[9] is at $d=2$ for this Hamiltonian.

B. Isotropic doublet

The behavior described by the Hamiltonian (10) is more complex and initially the isotropic case for which $f = v = 0$ will be considered. The propagator can then be written as

$$G_0^{\alpha\beta}(\vec{q}) = \left(r_0 + \vec{q}^2 + g_0 \frac{q_z^2}{q^2}\right)^{-1}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{\vec{q}^2}\right). \tag{14}$$

The differential recursion relations can then be obtained using the formulas of Aharony[9] and of Aharony and Fisher[8] to give to lowest order in u_l

$$\frac{dg_l}{dl} = 2g_l \tag{15}$$

and

$$\frac{du_l}{dl} = u_l - 18A(g_l)u_l^2, \tag{16}$$

where

$$A(x) = 2\pi \int_0^{\pi} \frac{\sin\theta\, d\theta}{(1 + x\cos^2\theta)^2}.$$

The recursion relation for g_l yields $g_l = g_0 e^{2l}$ so that $g_l \to \infty$ as $l \to \infty$. For large x the integral becomes

$$A(x) = \pi^2/(4x)^{1/2}.$$

With the aid of this expression and the result for g_l, the equation for u_l may be integrated to give

$$u_l = Ke^l/(l_0 + l), \tag{17}$$

where $l_0 = K/u_0$ and $K = g_0^{1/2}/9\pi^2$.

This result is the same as that obtained by Aharony[9] for the uniaxial dipolar case apart from the numerical factor K. The behavior is then similar; namely, the critical behavior is described by classical exponents and the transition temperature occurs when $r_0 = 0$. There are, however, logarithmic corrections which for the correlation length ξ and susceptibility χ have the form

$$\chi \propto \xi^2 \propto (T - T_0)^{-1} |\ln(T - T_0)|^{1/3}.$$

C. Anisotropic doublet

When anisotropy in the (xy) plane is allowed, as is always the case in real crystals, the parameters f and v in Eq. (10) are not zero. The propagator, Eq. (14), then becomes

$$G_0^{\alpha\beta}(\vec{q}) = \left(r_0 + \vec{q}^2 + g_0 \frac{q_z^2}{\vec{q}^2} + f_0 \frac{q_x^2 q_y^2}{\vec{q}^2}\right)^{-1}\left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{\vec{q}^2}\right).$$

The differential recursion relations for u_l and v_l are then

$$\frac{du_l}{dl}=u_l-\tfrac{1}{2}(6u_l+3v_l)^2B(g_l,f_l)$$

and

$$\frac{dv_l}{dl}=v_l-v_l(12u_l+9v_l)B(g_l,f_l)\,,$$

where $B(x,y)$ is the integral given in Eq. (13).

As yet we have been unable to obtain a solution to these recursion relations. In part this is because the recursion relation for f_l is complex and involves some integrals which are not readily evaluated. Even when the anisotropy in the propagator, f, is neglected the solution to the recursion relations has not been obtained.

The recursion relations may be rewritten by changing the variables $u_l\to x_le^l$ and $v_l\to y_le^l$ and noting that for large g_l, $B\sim(g_l)^{-1/2}$ when

$$\frac{dx_l}{dl}=-\tfrac{1}{2}(6x_l+3y_l)^2B'(f_l)\,,$$

$$\frac{dy_l}{dl}=-y_l(12x_l+9y_l)B'(f_l)\,.$$

where $B'(f_l)=B(g_l,f_l)e^l$. Since B' is positive dx_l/dl is negative. Further, since the condition for the quartic terms to give a continuous phase transition is $u_l+v_l>0$ and $2u_l+v_l>0$ the second recursion relation gives that $d|y|/dl$ is negative. In order for these equations to lead to logarithmic corrections x_l and y_l should decrease to zero as some power of l. Unfortunately, there appears not to be a consistent solution with this property. Since the recursion relation for x_l shows that x_l always decreases it seems most likely that as $l\to\infty$ that x_l will become negative and then y_l will decrease until the transition becomes of first order when $2y_l+v_l<0$.

We are unaware of any real system for which the phase transition is described by this model, so it might seem inappropriate to devote much effort to its solution. On the other hand, a very similar problem is that of the anisotropic cubic dipolar systems of which there are many examples which show large cubic anisotropies and first-order phase transitions. Behavior which is different from that predicted theoretically for the isotropic dipolar system.[8] Since the above problem is very similar but somewhat simpler than the full dipolar problem, a solution might well provide insight into the role of anisotropy in cubic dipolar systems.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

The behavior of acoustic waves at structural phase transitions has been reviewed by Rehwald.[2] In this paper we are concerned with materials which have a linear coupling between the order parameter and the acoustic waves. There are several examples of cubic materials which undergo phase transitions to a tetragonal structure accompanied by a softening of the elastic constant $c_{11}-c_{12}$. In the case of Nb_3Sn both ultrasonic and neutron scattering[7] measurements show that $c_{11}-c_{12}$ decreases to a very small value at the transition temperature and that the temperature dependence of the elastic constant is described by classical theory. Similar results are found in In-Tl alloys by Gunton and Saunders.[10] From Table I it is seen that these transitions are expected to be of first order because there is a cubic invariant allowed in the Hamiltonian. In both of these examples the third-order invariant must be small in magnitude, as the phase transitions are close to continuous. In the absence of the third-order invariant Table I shows that this type of transition

TABLE II. Properties of ferroelectrics which are piezoelectric in the paraelectric phase.

Classes	Strains	Ferroelectric axis	Symmetry	Fluctuations	Cubic invariant
$\bar{6}$	$e_1=-e_2, e_6$	x,y	E_2	II	Yes
622, $6mm$ $\bar{6}m2$, 6	e_4, e_5	x,y	E_1	II	Yes
32, $3m$	$e_1=-e_2, e_4$ e_5, e_6	x,y	E	0	Yes
$\bar{4}2m$	e_6	z	B_2	I	No
$\bar{4}2m$, 4, $\bar{4}$	e_4, e_5	x,y	E	II	No
$\bar{4}$	e_6	z	B	0	No
222	e_6	z	B_1	I	No
222, $2mm$	e_5	y	B_2	I	No
222, $2mm$	e_4	x	B_3	I	No
2	e_4, e_6	x,y	B	0	No
m	e_4, e_6	z	B	0	No

would be governed by classical exponents whereas the isotropic $n=2$, $d=3$ system has nonclassical exponents. The temperature dependence of the elastic constants observed in these systems lends support to our analysis.

Another class of materials which exhibit elastic instabilities are ferroelectric materials in which the material is piezoelectric in the paraelectric phase. In Table II are listed the crystal classes and symmetry properties of these phase transitions. In those cases where the transition is continuous and where the mode is a singlet, the theory predicts that the critical behavior will be classical without logarithmic corrections. In contrast, the theory of uniaxial ferroelectrics which are not piezoelectric predicts classical behavior with logarithmic corrections.[9] When the ferroelectric order parameter is a doublet, E modes in tetragonal classes, the behavior expected is classical with possibly logarithmic corrections or a first-order transition whereas for nonpiezoelectric ferroelectrics the behavior to be expected is nonclassical.[11] The result of the coupling to the acoustic waves is therefore to decrease the effect of the fluctuations, and to suppress the dimensionality separating classical from nonclassical behavior by one from that in nonpiezoelectric ferroelectrics. These results seem to be at least qualitatively in accord with the available measurements on these materials. In KH_2PO_4 the ferroelectric mode has B_2 symmetry and the transition is almost continuous. The exponents are found to be classical[12,13] and there has been no report of logarithmic corrections. In other piezoelectric ferroelectrics such as Rochelle salt less-detailed measurements[14] are available, but the transitions are of first order and consistent with classical behavior.

The Jahn-Teller systems also show acoustic wave instabilities, as described in the review by Gehring and Gehring.[15] These materials have the symmetry $4/mmm$ at high temperatures. In $DyVO_4$ the B_1 mode is strongly temperature dependent[16] and its temperature dependence is consistent with classical theory as is the behavior of the specific heat.[17] In $TmVO_4$ and $TbVO_4$ the elastic constant c_{66} is strongly temperature dependent[18,19] while in the former case the specific heat as a function of temperature is also given accurately by mean field theory.[20] These results are in excellent agreement with the predictions for instabilities against B_1 and B_2 distortions in this crystal structure.

In conclusion we have shown that Landau theory is to be expected to provide an excellent account of the statics of structural phase transitions in which a homogeneous deformation is a primary order parameter. The only possible exceptions are for the E distortions of tetragonal classes for which there may be either logarithmic corrections to Landau theory or a first-order transition and for $L=2$ transitions of isotorpic systems for which a first-order transition is predicted, but the fluctuations would be nonclassical if the transition was continuous. It would be of interest to investigate transitions of these types further theoretically and experimentally if examples could be found. The other surprising result is that in some cases continuous phase transitions may occur even though no fluctuations are possible for wavelengths shorter than the crystal dimensions.

Since mean field theory is predicted to give a good amount of the statics of these phase transitions it is reasonable to expect that anharmonic lattice dynamics will provide a reasonable account of the dynamics. There is always a difference between the elastic constants in the low-frequency or theormodynamic region from that in the high-frequency or collisionless region.[21] Consequently, whenever a phase transition is associated with an instability against an acoustic wave, types I and II above, the spectral response of the acoustic mode is expected to exhibit a central peak for the same reasons as discussed in detail for piezoelectric ferroelectrics.[22] Such a central peak has been observed in Nb_3Sn,[7] and in $TbVO_4$.[23]

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