Exploring phase transformations with neutron scattering

Analysis of neutron cross sections at various temperatures around the critical point allow us to view the process by which a substance transforms from one solid phase to another.

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Phase transformations have for many years intrigued physicists as dramatic and yet subtle phenomena for study. In the early 1960's came the belated realization that there exists a particularly simple mechanism responsible for a certain class of structural transformations in solids. This mechanism involves an instability in a mode of vibration of the solid; that is, a "soft phonon" (one of low energy) is said to "condense" into the lattice to cause the phase transformation. The process is susceptible to experimental study even in complex structures and has given us a handle on the dynamics of this cooperative phenonenon. Here we will discuss such phase transformations, which have come to be called "displacive transformations," and what can be learned about them by inelastic neutron-scattering experiments.

The passage of time has seen increasingly sophisticated techniques (both theoretical and experimental) brought to bear on phase transformations and a growing appreciation that the central questions are fundamental to many problems with large numbers of degrees of freedom, problems that arise in field theories as well as the study of condensed matter.[1] The complexity inherent in the description of cooperative phase transformations has caused much of the more fundamental interest in solid-state phase transformations to be concentrated on relatively simple mathematical models, which are most nearly realized in magnetic systems. Of course, transformations involving structural rearrangements of the constituent atoms in solids have been known from the earliest solid-state studies and are understood more or less thoroughly from thermodynamic and crystallographic points of view. But probably because the technologically interesting and thus most extensively studied examples tended to be structurally complex, for a long time structural phase transformations attracted little fundamental interest.

It is necessary to define a generalized displacive phase transformation and this is done by reference to the concept of an *order parameter*, some quantity that is nonzero in one of the phases but vanishes in the other. We do this with what may be called the "phonon expansion,"

$$\mathbf{u}_{lk}(t) = \sum_{\mu=(q,j)} \xi_{k\mu} Q_\mu(t) \exp i\mathbf{q}\cdot\mathbf{R}_l \quad (1)$$

which states that the displacement $\mathbf{u}_{lk}(t)$ of the kth atom in the lth unit cell from some given reference position can be written as the sum of plane waves with polarization vector ξ, amplitude $\mathbf{Q}(t)$, and wave-vector $\mathbf{q}$. Although originally concocted to describe lattice vibrations (in which case $\mathbf{Q}_\mu(t)$ has a harmonic time dependence) there is no reason why such an expansion cannot also be used to describe static displacements, leading to static components of $\mathbf{Q}$. Let a displacive transformation be one in which the order paramenter can be chosen as the static component of such a normal phonon coordinate. In order to describe the structure that results when such a set of static displacements becomes incorporated into the lattice, we may say by analogy with superfluid condensation that a phonon has condensed out. See figure 1, which shows a displacive transformation that occurs in strontium titanate, and the box on page 34, which describes a one-dimensional model of a displacive transformation.

Soft phonon modes

To study the dynamics of a phase transformation, we must look at the time-dependent fluctuations in the order parameter. These fluctuations form some sort of excitation of the solid and, in the present case, these excitations are just the phonons themselves. Furthermore, we know that near a second-order transformation, the amplitude of the fluctuations must diverge. Because the amplitude of a harmonic oscillator is inversely proportional to its frequency, we are led to the conclusion that the frequency of the phonons must tend towards zero at a second-order phase transformation. The physics of the situation is of course clear, because the frequency of a harmonic oscillator is a measure of the restoring force for the displacement; if this restoring force tends towards zero the displacements become free to incorporate themselves into the static structure.

How do these low-frequency temperature-dependent phonon modes, "soft modes" as they are called, come about? It is an anharmonic effect and, therefore, a difficult many-body problem, but we can get some idea of what is going on as follows. The potential energy of a lattice can be expanded in a power series in displacement starting with terms in u^2, then u^3, and so on. If the displacements are expressed in

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terms of normal coordinates in equation 1, then if for simplicity we neglect the cubic term, the potential energy is

$$V = \sum_{\mu} \frac{1}{2}\omega_{0\mu}{}^{2}Q_{\mu}{}^{2} + \sum_{\kappa\lambda\mu\nu} V(4)_{\kappa\lambda\mu\nu} Q_{\kappa}Q_{\lambda}Q_{\mu}Q_{\nu} + \cdots \quad (2)$$

where ω_0 is the bare phonon frequency. This expression simplifies if we ask for the mean potential experienced by the μth normal mode,

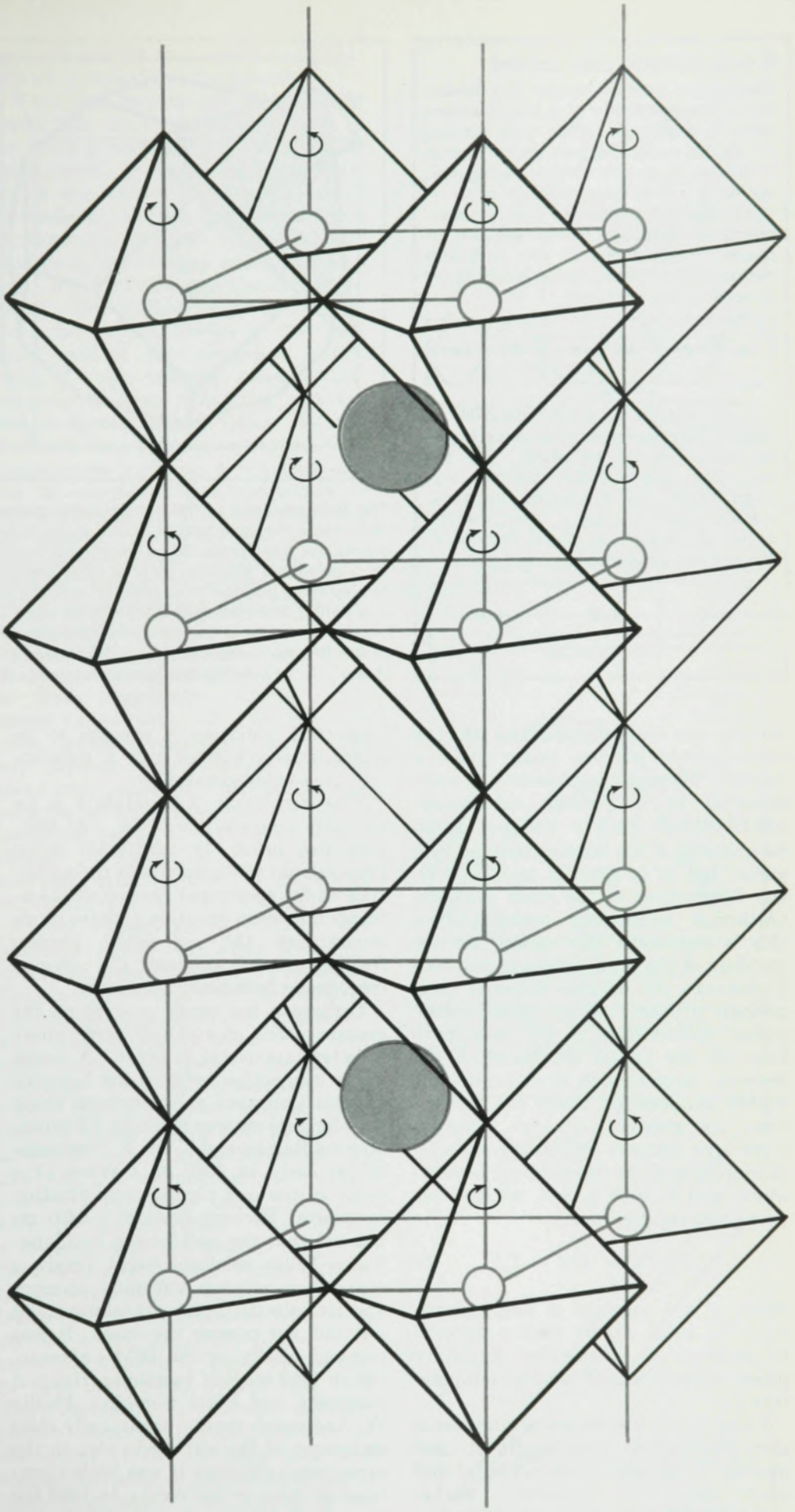
$$\langle V\rangle_{\mu} = \frac{1}{2}\omega_{0\mu}{}^{2}Q_{\mu}{}^{2} + \sum_{\kappa} V(4)_{\kappa\kappa\mu\mu}\langle Q_{\kappa}{}^{2}\rangle Q_{\mu}{}^{2} + \cdots \quad (3)$$

where the cross products between normal coordinates of different modes have disappeared because, at least to lowest order, normal modes are independent. Equation 3 has a harmonic part $\omega_{0\mu}{}^{2}Q_{\mu}{}^{2}$ plus another part contributed by the fluctuations from all the other modes in the system. But both of these contributions are proportional to the square of the normal coordinate of the mode itself, and therefore we can define a quasi-harmonic frequency

$$\Omega_{\mu}{}^{2}(T) = \omega_{0\mu}{}^{2} + \sum_{\kappa} V(4)_{\kappa\kappa\mu\mu}[2n(\omega_{\kappa}, T) + 1] + \cdots \quad (4)$$

where we have used the well known identity for the mean square thermal amplitude and where $n(\omega_\kappa, T)$ is the occupation number.

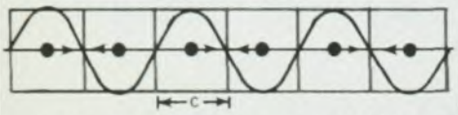
In normal materials at not too high temperatures, the harmonic part of equation 4 is always considerably greater than the anharmonic part, which supplies a small temperature-dependent correction. However, occa-



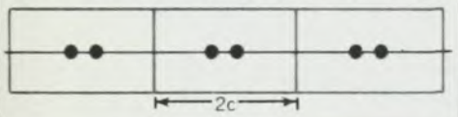
The structural phase transformation that occurs in strontium titanate ($SrTiO_3$). The strontium atoms are represented by the dark circles and the titanium atoms are represented by the open circles. The oxygen atoms are located at the vertices of the octahedra surrounding the titanium atoms. Shown here are two complete unit cells of the lattice. The structural transformation consists of rotations of the oxygen octahedra in alternating directions about the cubic crystal axes. The "soft phonon" that condenses to form the displacive transformation has a wave vector that lies at the (111) corner (R-point) in the Brillouin zone.
Figure 1

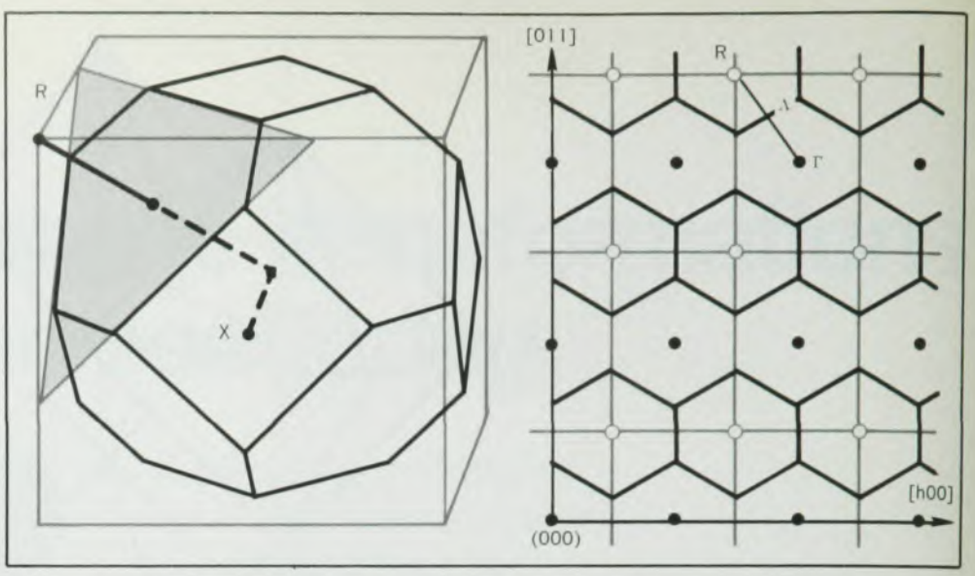
A one-dimensional model

We picture here a simple one-dimensional representation of a displacement wave in a periodic lattice with spacing c. In this case, the polarization vector ξ (arrow) is parallel to the propagation vector q. The magnitude of $\mathbf{q}$ ($q = \pi/c$) has been chosen so that displacements of adjacent atoms are out of phase. Fluctuations of this sort with harmonic time dependence are Brillouin zone-boundary phonons.



If the phonon suffers an instability, a static displacement or displacive transformation can be the result. For the particular zone-boundary phonon pictured above, the associated displacive transformation causes a "dimerization" of the lattice particles and a doubling of the unit cell dimension as shown below.





The Brillouin zone of the simple cubic perovskite lattice (grey lines) is on the left. This represents the structure of $SrTiO_3$ in its high-temperature phase. At about $T = 110$ K the substance transforms into a tetragonal form that has a representation in reciprocal space as a polygonal Brillouin zone of body-centered type (black lines). One face of the low-temperature polygon is shaded to indicate that it lies on the perpendicular bisector of the line joining the center of the Brillouin zone Γ to the point R. The point X lies on another one of the faces of the Brillouin-zone polygon. The figure on the right is a cross section of the Brillouin zone containing reflections of the [hkk] type often studied by neutron scattering. Λ denotes the line joining the points R and Γ. Figure 2

sionally one finds materials in which a very delicate balance exists where a *negative* harmonic contribution is compensated by a positive anharmonic contribution. Such a material would be unstable if the lattice could be held static, but it is actually stabilized by the fluctuations of the other phonons. (Although admittedly oversimplified, this is essentially the reason[2] for the stability of the solid phases of helium.) Sometimes the balance becomes more delicate still, and the zero-point anharmonic contribution is not enough to stabilize the lattice configuration but becomes large enough to do so at some higher temperature where the fluctuations are greater. At high temperatures, the phonon occupation number is proportional to the absolute temperature, and in such a case, we may approximate equation 4 as

$$\Omega_\mu^2(T) = \alpha(T - T_0) \qquad (5)$$

where α is a constant of proportionality. We could expect such a material to undergo a second-order displacive phase transformation at the temperature T_0.

Using much more careful arguments than given above (one should at least include third-order anharmonicity[3] and worry about *self consistency* rather than replacing $\langle Q_\kappa^2 \rangle$ by its harmonic average[4]) one can still arrive at soft-mode frequencies governed by equation 5. It is in fact the result of a mean field theory. We know that the results of mean field theories are only qualitatively correct at best for magnetic systems. But for many structural transformations equation 5 appears to be quantitatively correct over a substantial range of temperatures.

This derivation of equation 5 is for the high-temperature phase. At temperatures below T_0 additional terms proportional to the square of the amplitude of the condensed phonon displacements appear in equation 4; these terms renormalize the soft-mode phonon frequency, and prevent the phonon frequencies from being imaginary.

Perhaps a few words concerning the genesis of the idea of soft-mode phase transformations are in order. A rather vague connection between the behavior of optical phonons and structural phase transformations was made by Chandrasekhara Raman and T. M. K. Nedungadi[5] as early as 1940 as a result of a study of the α–β phase transformation in quartz; Herbert Frolich[6] (1949) remarked that the well known Lyddane–Sachs–Teller relation might imply a connection between soft-optic phonons and ferroelectric phase transformations but did not pursue the idea. It was pursued briefly at the IBM Laboratories in 1958 by Rolf Landauer, Hellmut Juretsche and Peter Sorokin. Phillip W. Anderson[7] gave a particularly clear statement of the soft-mode idea in the same year, although it was little circulated at least in the West. In 1959 the connection between ferroelectricity and soft modes occurred to William Cochran, and recognizing its importance, he elaborated on the idea in a series of papers[8] that simultaneously established and to a great extent shaped the subsequent developments in this field of study. The first confirmatory experiments[9] followed very soon thereafter.

Although historically the idea of a displacive phase transformation was first applied to ferroelectrics, it is clear from the more general definition of a displacive transformation given above that displacive ferroelectrics comprise a rather special subset of the general case. A ferroelectric must involve a condensation of a phonon that is both polar and of long wavelength because the ferroelectric state must have a macroscopic polarization. Clearly, in any material there are many more phonons without these special properties than there are with them and they are capable of becoming unstable also, so that one might expect to find more examples of nonferroelectric displacive transformations than ferroelectric ones. That this is not presently the case is at least partly due to the fact that ferroelectrics have a divergent macroscopic property, namely the dielectric response, to signal the occurrence of the transformation. Short-wavelength phonon instabilities are rather more subtle. Nevertheless some of these generalized displacive transformations illustrate the expected dynamical effects more clearly than any of the ferroelectric transformations thus far studied. In fact, the very first short-wavelength phonon instability to be established, in strontium titanate ($SrTiO_3$), is a nearly perfect example.

Strontium titanate

The first indication of a phase transformation in strontium titanate came from the observation of discontinuous behavior of the elastic constants,[10] and

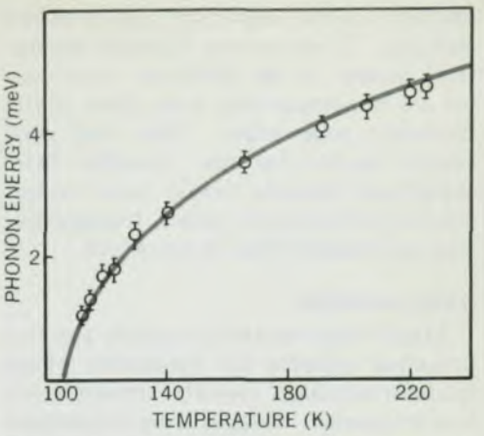
subsequent x-ray and optical work[11] established that at about 110 K strontium titanate transforms from a high-temperature cubic perovskite form into a low-temperature tetragonal form with the ratio of the lengths of the a and c axes differing from unity by less than one part in 10^3. Because the transformation is such a slight one and also because, as we shall see, it principally involves only oxygen motion for which there is very little scattering power, there was no immediate x-ray crystallographic evidence concerning the nature of the internal atomic rearrangements. Some five years after the transformation was discovered, H. Unoki and T. Sakudo proposed a structure based upon their study of the splitting of the electron spin resonance spectrum of paramagnetic impurities.[12] The displacements they proposed consist of rotation of the oxygen octahedron surrounding every titanium ion about a [100] axis (see figure 1). However, since the oxygen atoms are shared between octahedra, the sense of the rotation alternates as one passes between adjacent unit cells. The new unit cell has twice the volume of the original cubic one.

Once the atomic displacements are known, a very practical test due to Cochran and A. Zia[13] determine whether or not one is dealing with a displacive transformation. For if the low-temperature phase does indeed represent the condensation of a single normal phonon mode then the static displacements should have all of the symmetry properties of the condensed phonon, about which certain well defined group-theoretical statements can be made. If one does indeed find a one-to-one correspondence between the symmetry properties of the static displacements and a single normal phonon mode, the implication is certainly strong that that mode is involved in a transformation and is thus soft.

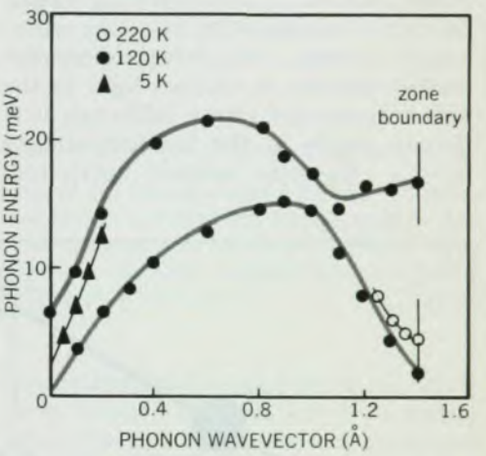
Paul Fleury, James Scott, and John Worlock[14] realized that Unoki and Sakudo's proposed displacements did indeed represent a single normal phonon and that the wave vector of the phonon was such that it lay at the [111] corner of the simple cubic Brillouin zone. This is a special point of very high symmetry in the reciprocal lattice, and is known as the "R point." (It is easy to see that the wave vector involved must be at the edge of the Brillouin zone, for it is only for such wave vector that the displacements reverse on passing from one unit cell to the next. The one dimensional phonon depicted in the box on page 34 provides a good example). Fleury and his colleagues were also able to show that certain puzzling features of the light-scattering spectrum of $SrTiO_3$ could be explained as a result of the change in unit-cell volume that would accompany such an atomic rearrangement.

What was lacking was direct verification that there was a soft phonon in the cubic phase with a wave vector at the R point. Inelastic neutron scattering is the only technique by which spectroscopy on such short-wavelength excitations is possible. Figure 2 shows, in more detail, changes in the Brillouin zone implied by the Unoki–Sakudo model. The Brillouin zone of the simple cubic lattice, shown by the gray lines, enclose the reciprocal lattice point, Γ. By erecting perpendicular bisectors between this point and the new reciprocal lattice points, R, the Brillouin zone appropriate to the low-temperature structure is obtained and can be recognized as a polyhedron of the body-centered type, showing that the direct lattice of the new phase is face-centered cubic. (The slight spontaneous strains mentioned earlier, which accompany the transformation, are ignored here.) The proper scattering experiment obviously concentrates on scattering vectors that correspond to these superlattice vectors. We would expect that, at high temperatures, inelastic scattering due to the soft phonon modes would be seen about such points but that as the temperature is lowered toward the phase transition, part of the scattering should change to elastic Bragg scattering. Just such behavior was seen by groups at Brookhaven[15] and Chalk River.[16]

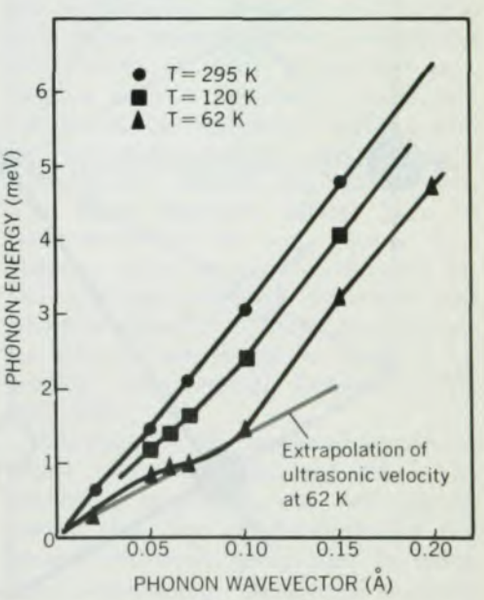
Figure 3 shows the temperature dependence of the soft-mode frequency above the transformation temperature. The data were obtained by standard inelastic neutron-scattering techniques, with what is known as a triple-axis spectrometer (see cover). In this instrument both the momentum and energy of the incident and scattered neutron beams are defined by diffraction from crystal monochomators. In this way the momentum and energy transfer to a sample under study can be systematically varied. The data are consistent with the simple molecular field ideas given above. Figure 4 shows the dispersion curves for the two lowest transverse phonon branches with wave vectors along the [111] direction in strontium titanate. These curves can be best understood by realizing that they represent a normal acoustic branch starting at zero frequency at the center of the Brillouin zone and ending as the upper branch at the Brillouin zone edge. The optical mode, however, has quite an anomalous behavior. Its frequency is low and temperature dependent both at the center of the Brillouin zone and at the Brillouin zone edge, and it rises to a maximum in the interior. Because the two branches have the same symmetry properties, they interact and repel one



Temperature-dependent phonon energy in $SrTiO_3$. The solid curve is the prediction of mean field theory for the energy of "soft mode" zone-boundary phonons $(\hbar\omega)^2 = \alpha(T - T_0)$ where α is the constant of proportionality and T_0 is the critical temperature. The wave vector of these phonons is $\mathbf{q} = (1/2, 1/2, 1/2)$. The data were obtained in inelastic neutron scattering experiments. Figure 3



Dispersion curve of the lowest transverse phonons in $SrTiO_3$. The wave vectors lie along the (111) direction. Figure 4



Dispersion curves for the soft (111) transverse acoustic phonon in Nb_3Sn. The ultrasonic velocity, given by the slopes of these curves, continues to decrease with temperature until it reaches nearly zero at 45 K. Nb_3Sn is a superconductor. Figure 5

another in the region of the nominal crossing. In strontium titanate the optical modes at the Brillouin zone center are in competition with those at the Brillouin zone edge. Had the zone center modes become unstable first, strontium titanate would have undergone a ferroelectric phase transformation, as it nearly does in any event.

Other materials

Many other materials satisfy the two principal criteria for displacive phase transformations, namely anomalously low-frequency temperature-dependent phonon response in the high-temperature phase, and condensation of these same phonon-like displacements into the low-temperature structure. Table 1 is a representative list of such materials that have been studied by neutron scattering. While for the ferroelectrics neutron spectroscopy is in a sense a supplement to less expensive and faster optical spectroscopy, the α–β quartz transformation is an interesting example of the condensation of a long-wavelength phonon, which by symmetry neither absorbs or scatters light in the high-temperature phase (although it is Raman active in the low-temperature phase). Inelastic neutron scattering, with much less stringent selection rules, has established strong inelastic critical scattering near the transformation temperature.[17] In this instance, as in many others as well, the actual transformation occurs at a slightly higher temperature than that at which the soft phonon frequency goes to zero, and the order parameter, rather than increasing continuously from zero, assumes a small nonzero value abruptly at the transformation temperature and then grows smoothly as the temperature is further lowered. It is useful to think of these transformations, characterized by large critical fluctuations, but with a finite discontinuity in the order parameter as being "nearly" second order.

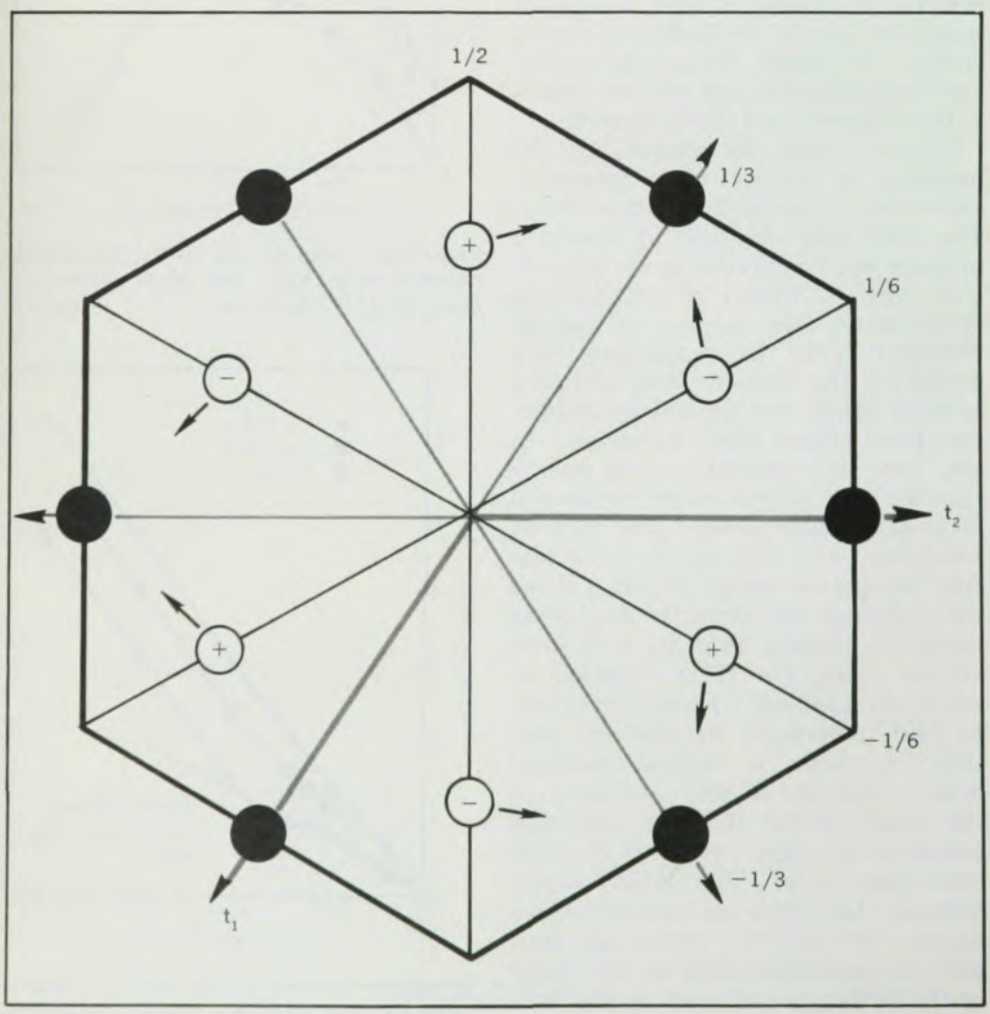
Two materials that have the β-tungsten structure, Nb_3Sn and V_3Si, undergo an acoustic phonon instability. The mode softening in this case takes the form of the velocity of sound tending to zero for a particular propagation direction. The results[18] of the neutron-scattering investigation of the dispersion of the soft acoustic phonon in Nb_3Sn are shown in figure 5. The extent to which this softening extends to short wavelengths was of considerable interest in connection with the extraordinarily high temperature at which Nb_3Sn becomes superconducting. High superconducting transformation temperatures are favored by low phonon frequencies, and if the extreme softening observed in ultrasonic experiments had extended appreciably to shorter wavelengths they could have completely dominated the superconducting electron-pairing interaction.

The rare earth molybdates, listed in Table 1 as "ferrielectric," provide an interesting example of the way nature can embellish the simple soft-mode picture. These materials are ferroelectrics in the sense that they develop a reversible macroscopic polarization below a well defined transformation temperature. But the lack of a substantial enhancement of the dielectric response normally associated with ferroelectric transformations puzzled investigators for many years. Following a suggestion by Erling Pytte,[19] a neutron-scattering investigation revealed soft-mode behavior not in a long-wavelength polar phonon as one should expect for a ferroelectric, but rather in short-wavelength phonons (the wave vector at the edge of the Brillouin zone).[20] The atomic displacements that result from this phonon condensation reverse this direction in adjacent unit cells; so it is obvious that this does not give rise to a ferroelectric moment.

Perhaps the simplest way to understand this behavior is to write an expression for the free energy, using L. D. Landau's idea of a power series expansion in the order parameter.[21] The only new idea is that we must be dealing with two distinct order parameters, $\langle Q_{ZB}\rangle$ representing the short-wavelength zone-boundary phonon condensation observed in the neutron-scattering experiment, and another $\langle Q_0\rangle$ responsible for the macroscopic polarization. Simplified to bare essentials the appropriate free energy is of the form

$$F = \left[\frac{1}{2}\Omega_{ZB}^{\,2}\langle Q_{ZB}\rangle^2 + \frac{1}{4}V(4)\langle Q_{ZB}\rangle^4 + \cdots\right] + \frac{1}{2}\Omega_0^{\,2}\langle Q_0\rangle^2 + V(3)\langle Q_{ZB}\rangle^2\langle Q_0\rangle + \cdots \quad (6)$$

The bracketed terms represent the "harmonic" and higher-order contributions to the zone-boundary phonon condensation. The soft-mode frequency, $\Omega_{ZB} \to 0$ near the transformation temperature. The next term is the leading "harmonic" contribution to the $\langle Q_0\rangle$ condensation energy, and the absence of a strong dielectric anomaly establishes that Ω_0 has no strong temperature dependence. The final term is a third-order anharmonic coupling of the two order parameters having the form required by symmetry. By minimizing this free energy we find that (so long as $V(3)$, $V(4)$ are sufficiently positive) the high-temperature solution $\langle Q_{ZB}\rangle = \langle Q_0\rangle$



A projection on the basal plane of the Wigner–Seitz unit cell of β-quartz. The silicon atoms are represented by the dark circles and the oxygen atoms are represented by the open circles. The arrows indicate the shifts in the atomic positions between the β-phase and the room-temperature α-phase. Figure 6

= 0 is replaced by a low-temperature solution with $\langle Q_{ZB} \rangle \neq 0$ if $\Omega^2_{ZB} < 0$. Although the transformation is driven by the soft mode Q_{ZB}, there is an induced ferroelectric condensation, $\langle Q_0 \rangle$ caused by the anharmonic coupling and given by the extremum condition

$$F_\mu(\mathbf{Q}) = \sum_{\kappa}^{\text{unit cell}} (\mathbf{Q} \cdot \xi_{\kappa\mu}) f_\kappa(\mathbf{Q}) \exp i\mathbf{Q} \cdot \mathbf{R} \quad (7)$$

The concept of a primary driving order parameter, which exhibits critical fluctuations as opposed to secondary (driven) order parameters with no soft mode or enhanced fluctuation spectrum, is very useful in discussing other solid-state phase transformations as well. (It is interesting to note that the preceding discussion is a counter example to Landau's theorem that two order parameters of different symmetry cannot arise at the second-order transformation. Landau evidently did not consider the effect of higher-order coupling terms, and his conclusions remain true only for what we term primary order parameters).

Dynamic crystallography

A prediction of the "soft-mode" theory of structural transformations that was touched upon previously is the similarity of the static atomic displacements occurring in the transformation to the fluctuating displacements associated with the unstable soft mode. It would be of considerable interest to test this aspect of the theory, and fortunately this is possible with neutron scattering.[17,22]

The total scattering due to creation or annihilation or both of phonons in a vibrational mode μ with momentum transfer $\hbar\mathbf{Q} = \hbar(\mathbf{k}_0 - \mathbf{k}')$ is proportional to the square of an inelastic structure factor

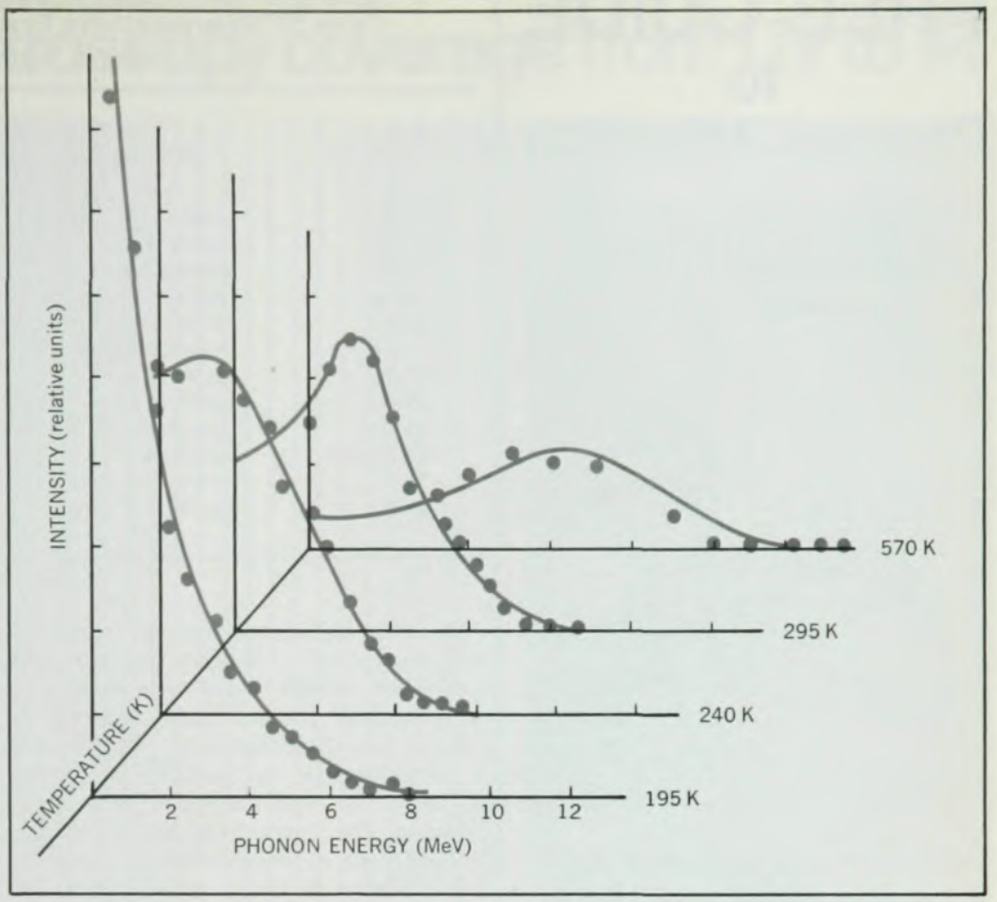
$$\frac{\partial F}{\partial \langle Q_0 \rangle} = \Omega_0^2 \langle Q_0 \rangle + V(3) \langle Q_{ZB} \rangle^2 = 0.$$

where $\xi_{\kappa\mu}$ is defined in equation 1, $f_\kappa(\mathbf{Q}) = b_\kappa \exp[-W_\kappa(\mathbf{Q})]$ is the coherent scattering length of the κth nucleus in the unit cell, modified by a Debye–Waller factor. $\mathbf{R}$ is the equilibrum position of the κth nucleus relative to the origin of the unit cell. The wavevector $\mathbf{q}$ of the phonon involved can always be taken to lie within the first Brillouin zone, that is, $\mathbf{Q} = \mathbf{G} + \mathbf{q}$ where $\mathbf{G}$ is a reciprocal lattice vector.

Note that the inelastic structure factor is just the familiar elastic structure governing Bragg scattering multiplied by the projection of atomic displacement along the scattering vector $\mathbf{Q}$. Thus, aside from $\xi_{\kappa\mu}$, all the quantities in equation 7 can be determined with reasonable precision by normal crystallographic methods. Thus, measuring the integrated scattering intensity of the same phonon at two different values of $\mathbf{Q}$ (but the same value of $\mathbf{Q} - \mathbf{G}$) is equivalent to measuring two different projections of the phonon displacement vector ξ_κ. This is the basis of the method of phonon-mode determination by inelastic neutron scattering, which was first emphasized by Bertram N. Brockhouse and his collaborators.[23] The biggest difficulty in practice is that normal phonon "reflections" are quite weak (down from Bragg reflections by approximately 10^{-4} to 10^{-5}) even with serious compromises in experimental resolution. Fortunately, this problem is considerably less severe for materials with soft modes, since the phonon scattering intensity is inversely proportional to the square of the phonon frequency. Figure 6 shows, for example, the atomic displacements that link the α and β forms of quartz. A comparison of the static displacement pattern determined by x rays[24] with the dynamic displacements obtained by analysis of soft-phonon intensities[17] show the two normalized displacement patterns to be identical to within the combined error of both determinations ($\approx 15\%$).

In addition to providing insight into the mechanism of specific phase transformations, the study of soft-phonon dynamics has proven interesting from another point of view. We can think of materials undergoing displacive phase transformations as having certain vibrational modes for which, probably through cancellation of attractive and repulsive terms, the net quasi-harmonic potential is unusually small and is moreover "tunable" with temperature. Because it is likely that this same cancellation process extends to the anharmonic terms as well, displacive phase transformations give us the opportunity to study vibrational excitations with a relatively small and manipulatable harmonic content, and as we might expect certain novel anharmonic effects are observable. The more dramatic effects seen to date occur in the soft phonon line shapes, which reveal considerable detail into the processes by which soft phonons decay[23]. These line shapes for $KMnF_3$ are shown in figure 7 for several temperatures between 572K and 194K.

Although by no means all structural phase transformations are driven by anything resembling a soft-phonon mode, this line of development has proved extremely useful and its influence is spreading. Structural transformations that involve discrete displacements between rather widely separated minima in the atomic single-particle potentials are now being discussed in terms of cooperative soft-tunneling excitations.[26] Certain magnetic struc-



Temperature dependent changes in the line shape of the phonon responsible for the phase transformation in $KMnF_3$. As the temperature is lowered toward the transformation temperature (185 K), well defined phonon sidebands collapse into the origin giving a single peaked response. Similar behavior is observed with a viscously-damped harmonic pendulum as the ratio of the restoring forces to the damping forces are varied. Figure 7

Table 1. Representative Examples of Displacive Structural Phase Transformations

Material	Structure	Wave vector	Type	T_0(K)
$BaTiO_3$	cubic	0	ferroelectric	400
$PbTiO_3$	perovskite	0	ferroelectric	765
$LiNbO_3$	hexagonal	0	ferroelectric	1460
$LiTaO_3$	Al_2O_3	0	ferroelectric	890
GeTe	cubic-NaCl	0	ferroelectric	670
Quartz	rhombohedral	0	non-polar	850
$SrTiO_3$	cubic	½ (111)	antiferroelectric	105
$KMnF_3$	perovskite	½ (111)	antiferroelectric	185
$LaAlO_3$	perovskite	½ (111)	antiferroelectric	810
$Gd_2(MoO_4)_3$	tetragonal	½ (110)	ferrielectric	430
V_3Si	cubic	$q \to 0$	elastic	21
Nb_3Sn	β-W	$q \to 0$	$(c_{11}-c_{12}) \to 0$	46

tural rearrangements appear to involve soft magnons.[27] Within the next few years we should begin to discover to what extent the soft-mode concept is useful in understanding Martensitic transformations in metals[28] and even perhaps the phenomenon of melting.[29] Finally, the connection between soft-modes and superconductivity touched upon earlier is being actively pursued at the present time.[30]

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