Regions of Incommensurability

Regions of Incommensurability in Phase Diagrams

By T. Janssen
Institute for Theoretical Physics
University of Nijmegen, Holland

and

J. A. Tjon
Institute for Theoretical Physics
University of Utrecht, Holland

A discussion is given of the basic properties of incommensurate crystal phases and their occurrence in phase diagrams. The origin of the phenomenon is illustrated on a simple model that reproduces the main characteristics. The resulting model phase diagram and a number of phase diagrams of materials with an incommensurate phase are described.

Long before 1900, the regularities in crystal forms were explained with the hypothesis that crystals are composed of identical building blocks. However, the theory of the possible crystal arrangements remained mathematical. The experimental verification of the hypothesis was not given before 1915, when von Laue showed by means of the just-discovered X-rays that crystals have a lattice of translations in three dimensions. Since then, the prevailing idea about the structure of matter at low temperatures has been that it has such a space group symmetry. Of course, other systems also were known, such as amorphous systems and crystals with defects, but these were considered as exceptions or as small deviations from an ideal structure.

The consequence of the space group symmetry of a crystal is that the spots of its diffraction pattern also form a lattice, the so-called reciprocal lattice. Deviations from such a pattern were known: apart from the "normal" reflections, temperature-dependent satellites were sometimes observed, but these were usually considered as perturbations. However, about twenty years ago it was shown that these satellites must be taken seriously; the reason is that there are "crystals" without space group symmetry. Nevertheless, explanation for calling them crystals is that a nearly perfect ordering over large distances often exists. Another argument is that the appropriate symmetry group can be shown as a crystallographic space group, not in three but in more dimensions.

The earlier examples of such structures could be considered as ordinary crystals (with space group symmetry), where all the atoms are displaced periodically from the regular crystal lattice. Therefore, these structures were called modulated crystals. Of course, when the periodicity of the displacements belongs to the lattice of the underlying ordinary crystal, a normal crystal is obtained, but with a larger unit cell; if the displacement in every third cell is the same, a crystal with a unit cell that is three times as large is obtained. Hence, to have another kind of cell is the same, a crystal with a unit cell that is three times as large is obtained. Hence, to have another kind of structure, the period of the displacements should not fit the periodicity of the lattice: both periodicities are incommensurate, whence the term "incommensurate crystal" also used. It was already known that such incommensurate crystals existed. It had been known that there are spin systems where the spin arrangement is in the form of a helix, whereas the wave length of this helix does not fit the periodicity of the spin positions. A careful analysis of these systems showed that, in such systems, the spin positions were affected by the helix structure of the spin orientations. In fact, the spin positions also form a modulated or incommensurate crystal.

In the last ten years, a large number of such systems have been discovered. Some of them are insulators, such as K$_2$SeO$_4$ or Na$_2$CO$_3$; others are conducting. To the latter class belong many systems with conduction mainly in one or two directions. An example is tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).

Also, quite different structures were found where the crystal cannot be described as a distortion of an ordinary crystal, but where the positions form (in first approximation) an ordinary crystal, with a certain probability for each site to contain one of two (or more) species of atoms. An example is the alloy CuAuII. The Cu and Au atoms are distributed over the sites of a side-centered orthorhombic lattice. In first approximation, there are domains that arise from the interchange of the roles of Cu and Au. A more precise description is provided, with a function giving the probability of finding Cu or Au on a certain site. This site-dependent probability is periodic, with a period that is roughly one-tenth of the reciprocal basis vector, $\vec{a}^*$ (see Fig. 1).

The systems mentioned until now also could be called modulated structures. This is no longer possible for another class: that of the composite crystals. An example is Hg$_{3-x}$AsF$_6$, in which the mercury atoms form chains in the channels of the host lattice formed by AsF$_6$ tetrahedra. There are two systems of parallel mercury chains, one in the $x$ and one in the $y$ direction. Both mercury systems and the AsF$_6$ system have ordinary space group symmetry, but because the lattice parameters are different, the whole does not have such symmetry. In the X-ray diffraction pattern, satellites are also seen, which is the reason they are identified as incommensurate crystals.

Incommensurate Crystal Phases

The spots of an X-ray diffraction pattern for an ordinary crystal can be labeled by three integers: the indices $h$, $k$, and $l$. An incommensurate crystal phase is detected from the diffraction if the spots have to be labeled with more than three indices; next to conspicuous main reflections, there are (sharp) satellites such that the positions of the spots are described by:

$$\vec{k} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \quad (Eq \ 1)$$

Bulletin of Alloy Phase Diagrams Vol. 3 No. 3 1982 281
For simplicity, it is assumed that one additional vector, \( \hat{q} \), is sufficient. Sometimes more than one, but at most a small number of them, are necessary. The fact that the spots are sharp means that there is ordering over large distances in the crystal.

This article is restricted to displacively modulated crystals; the displacements of the atoms are periodic. In the simplest example of a crystal with one atom per unit cell and a sinusoidal modulation, the positions of the atoms are given by:

\[
\hat{n} + \hat{u}_s = n_1 \hat{a} + n_2 \hat{b} + n_3 \hat{c} + \hat{d} \sin(\hat{q} \cdot \hat{n})
\]  
(Eq 2)

where \( \hat{a}, \hat{b}, \) and \( \hat{c} \) are basis translation vectors of the lattice. The structure factor for this crystal, which determines the intensity of the diffraction spots, is then given by the expression:

\[
F(\hat{k}) \approx \sum_{\hat{n}} \exp[-i \hat{k} \cdot (\hat{n} + \hat{d} \sin \hat{q} \cdot \hat{n})]
\]

\[
= \sum_{h,k,l,m} J_m(\hat{k} \cdot \hat{d}) \delta(\hat{k} - h\hat{a}^* - k\hat{b}^* - l\hat{c}^* - m\hat{q})
\]  
(Eq 3)

where \( J_m(x) \) is the m-th order Bessel function. Therefore, the periodicity of the displacements is exactly given by the inverse \( 2\pi/q \) of the modulation vector.

Incommensurate crystal phases often occur as an intermediate phase between two phases with an ordinary crystal structure. As an example, consider \( K_2 SeO_4 \). For temperatures above 128 K, the structure has space group \( Pnam \). Below 93 K there is a superstructure with an orthorhombic unit cell that is three times as large as the high-temperature unit cell. Between 93 and 128 K, the compound has an incommensurate crystal phase. The wave vector, \( \hat{q} \), is approximately (but not exactly) one-third of the reciprocal lattice vector \( \hat{a}^* \). The same happens in many materials. The temperature interval in which the incommensurate phase exists may be very large and very narrow; in \( Na_2 CO_3 \), it is roughly 500 degrees, whereas in \( NaNO_2 \) it is not more than 1.5 degrees. Moreover, there are also examples (biphenyl and \( ThBr_4 \)) where the incommensurate phase seems to go down to the lowest temperatures.

The phase transition from the high-temperature phase to the incommensurate phase at \( T = T_0 \) is often introduced by a so-called soft mode: one of the phonon branches of the crystal becomes strongly dependent on temperature. For \( T \) tending to \( T_0 \), the minimum frequency of the branch even goes to zero. This minimum occurs at a wave vector that is exactly the wave vector of the modulation that develops below \( T_0 \). This soft mode has not always been observed, but for many members of the \( A_2 BX_4 \) family there are strong indications for its presence.

In the incommensurate phase, the wave vector of the modulation starts at \( T = T_0 \) at the value of the wave vector of the soft mode. In many of the \( A_2 BX_4 \) materials, the wave vector stays constant or changes very little over a fairly large temperature interval, in contrast to, for example, a material such as \( NaNO_2 \), where the wave vector changes by 20% over 1.5 degrees. For lower temperatures, one approaches the transition to the low-temperature superstructure, the so-called lock-in transition at \( T_0 \), where the wave vector goes rapidly (or immediately jumps) to a commensurate value.

**Origin of Incommensurability: Model Studies**

In the last few years, insight into the mechanism that gives rise to the occurrence of incommensurate crystal phases has been gained. Globally, it may be stated that the reason is a competition of forces, each of which favors a different periodicity. Sometimes these forces are caused by subsystems. A well-known example is the Peierls distortion of a conducting one-dimensional chain. Peierls showed that such a system is unstable against the formation of a larger unit cell if the Fermi level is in the middle of a band. Overhauser showed that sometimes the state of lowest energy of an electron gas is not a uniform distribution, but waves develop in the charge density or in the spin density. Due to the coupling with the lattice, the latter obtains a periodic distortion with the same wave length as the density wave. Because this wave length, which is determined by the Fermi wave vector, is generally incommensurate with the lattice, the result is an incommensurate structure of the lattice.

It has been known for a long time that spin systems with nearest and next nearest neighbor interaction may show an instability with a wave vector in a general point of the Brillouin zone. Recently, an investigation showed what happens if the temperature is lowered below that at which the instability occurs. It has become clear that such systems may have very complicated structures, among which are incommensurate and chaotic states (Fisher and Selke, Bak and von Boehm). Just as in spin systems, crystals with different interaction between neighbors and between next nearest neighbors may have an instability in their phonon modes. A very simple model already showed the most characteristic prop-