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# INCOMMENSURATE STRUCTURES

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Incommensurate Structures

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Abstract. A review is given of neutron scattering studies of displacive incommensurate structures, and of the instabilities of crystalline solids that lead to their formation.

## 1. Introduction

Incommensurate structures are peculiar quasi-crystalline substances that lack periodic translation symmetry not in a haphazard amorphous way but because two (or perhaps more) elements of translational symmetry are present which are mutually incompatible. Suppose $A(\vec{r})$ and $B(\vec{r})$ represent the spatial distribution of two characteristic properties of a material and that

$$A(\vec{r}) = \sum_{\{G\}} A_G e^{i\vec{G}\cdot\vec{r}} \; ; \quad B(\vec{r}) = \sum_{\{G'\}} B_{G'} e^{i\vec{G}'\cdot\vec{r}} \qquad (1)$$

The structure is incommensurate if the sets of reciprocal lattice vectors $\{\vec{G}\}$ and $\{\vec{G}'\}$ have only the trivial elements $\vec{G} = \vec{G}' = 0$ in common. Various cases are possible depending on what A and B represent, as shown in Table 1.

Neutron scattering has been instrumental in the study of incommensurate structures of all of the above types, but this is particularly true for the magnetic case, since neutrons are uniquely sensitive to magnetic spatial distributions on an atomic scale. The essential role of competing forces (in this case due to magnetic exchange interaction) of various ranges was emphasized in the models of the phenomena. Major reviews by Mackintosh (1982) and by Koehler (1982) in this volume make further comment here unnecessary.

The history of incommensurate intergrowth/overgrowth structural studies with neutrons is, by comparison, brief. The study of adsorbed surface monolayers, which depended crucially on the advent of exfoliated graphite substrates is reviewed by Nielsen (1982) in the volume. The best studied example of an incommensurate intergrowth compound to date is $Hg_{3-\delta}AsF_6$. This material has many remarkable properties, not the least of which is that of a one dimensional liquid, and the results of neutron studies have been recently reviewed (Axe, 1982). The present review will concentrate

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Table 1

| Incommensurate Structure Type | A(r) | B(r) | Example |
|---|---|---|---|
| 1. magnetic | magnetic density, M | nuclear density, $\rho$ | Cr, r.e. metals |
| 2. compositional | average $\langle\rho_1+\rho_2\rangle$ | differential density, $\langle\rho_1-\rho_2\rangle$ | CuAuII, feldspars |
| 3. intergrowth/ overgrowth | lattice $\rho_1$ | lattice $\rho_2$ | adsorbed monolayers |
| 4. displacive | displacement field, $\vec{u}(\vec{r})$ | average | quasi-1d & 2d metals |

on the last of the four types, displacive modulation, which involves periodic displacements,

$$\vec{u}(\vec{r}) = \vec{A}\cos(\vec{q}\cdot\vec{r}-\phi) \qquad (2)$$

of the atoms away from an average regular lattice site. Not uncommonly the modulation amplitude, $\vec{A}$, disappears above a certain temperature, $T_o$, the material thereby transforming from an incommensurate structure into a commensurate (normal) phase with the average structure.

## 2. Charge Density Waves

In metals an incommensurate transformation may result from a charge density wave (CDW) instability in the conduction electrons near the Fermi surface. Neutrons couple not directly to the CDW but rather to the distortions that result as the atomic cores adjust by coulomb screening of the CDW. CDW instabilities are favored by large portions of the Fermi surface separated by the special wavevector, $\vec{q}_o$, (Fermi surface nesting) which is more probable for quasi-one- or two-dimensional metals, as the Fermi energy then becomes independent of some component(s) of the electron momenta. For reviews of neutron studies of quasi-one-dimensional metals see Comès and Shirane (1979). Additional interest in the study of these materials derives from the fact that there are strongly competing tendencies among the conduction electrons to form charge density waves, spin density waves and superconductivity. The successful culmination of the latter tendency has been recently confirmed in certain quasi-one-dimensional organic metals.

Of the various quasi-two-dimensional CDW systems, the 2H polytype of $TaSe_2$ has been the most thoroughly investigated. Early electron diffraction studies (Wilson et al. 1975) showed sattelite Bragg reflections appearing at $T < T_o = 123K$, and presumed to be commensurate with the average lattice. A subsequent higher resolution neutron study (Moncton et al. 1977) showed the sattelites to be incommensurate near $T_o$ with a temperature dependent wavevector, $\vec{q}_\delta=(1-\delta)\vec{a}^*/3$. Moncton et al. went on

to study the temperature dependent amplitude of the CDW and to discuss the mechanism for $\delta(T)$ and the "lock-in" transformation at $T_c$=90K below which $\delta(T)=0$. The latter discussion was extended by McMillan (1976). The key point to recognize is that purely sinusoidal modulation (eqn. 2 with constant $\phi$) cannot take advantage of the periodic potential of the average lattice. However with the proper spatial variation of $\phi(r)$ it is possible to produce large commensurate regions separated by narrow domain walls in which $\phi(r)$ changes rapidly. Model calculations suggest that under certain conditions an ordered array of these domain walls, which McMillan called discommensurations (D.C.'s) would be the state of lowest energy. The position of the dominant Bragg sattelite would be determined by the density of D.C.'s.

Figure 1 shows $\delta(T)$ as obtained in an even higher resolution study using x-rays by Fleming et al. (1980). In addition to confirming the lock-in transformation found with neutrons, the new study established the existance of two distinctly different incommensurate phases. The fully incommensurate phase obtained on cooling from high temperatures incorporates three incommensurate wavevectors directed along alternate 6-fold axes of the hexagonal reciprocal lattice with magnitude $q_\delta$. On warming from the commensurate phase an additional phase is found in which one of the three wavevectors remains commensurate. In terms of a real space description, the latter phase involves a parallel stripe D.C. pattern, whereas the former requires a hexagonal honeycomb array of D.C.'s. Direct confirmation of the D.C. model has come from recent dark field electron microscopy studies (Fung et al. 1981) and (Chen et al. 1981).

## 3. Dynamics

Neutron studies have also been instrumental in studying the dynamics of displacive incommensurate phase transformations. The form of the periodic displacement in eq. (2) suggest that we view the transformation as a condensation or "freezing-in" of a phonon with wavevector $q_o$, which migh occur because the phonon frequency $\omega(q_o)$ vanishes. Such "soft mode" transformations are reviewed by Cowley (1982) in this volume. In the case of a CDW transformation, the screening effects discussed previously can be reflected in $\omega(q_o)$ through giant Kohn anomalies (Kohn, 1959) which have been observed spectacularly in the quasi-one-dimensional metal KCP ($K_2Pt(CN)_6Br_x$). (Renker et al. 1974) and (Carneiro et al. 1976). Substantial, but incomplete phonon softening is observed in the quasi-two-dimensional CDW materials as well (Moncton et al. 1977). However, the best example of a soft mode incommensurate transformation occurs not in a CDW metal but rather in the insulator $K_2SeO_4$ (Iizumi et al. 1977) as shown in Fig. 2. This dispersion relation is essentially the Fourier transform of the interplanar forces, from which we can deduce that the instability in $K_2SeO_4$ results from anomalously large and temperature dependent forces between planes of atoms which are third-nearest neighbors. On a fundamental microscopic level, coulomb (dipolar) forces presumably play a decisive role, although model calculations are far from simple. (See, for example, Hague et al. 1978).

But what about the dynamics of the incommensurate phases themselves? Because it should be possible to add an overall phase shift to eq. 2 while leaving the energy unchanged it follows that there should appear a new type of gapless long wavelength excitation (a phason) which represents slow spatial variations in $\phi$ (Overhauser 1968). In the simple soft mode picture presented above the added presence of static displacements below

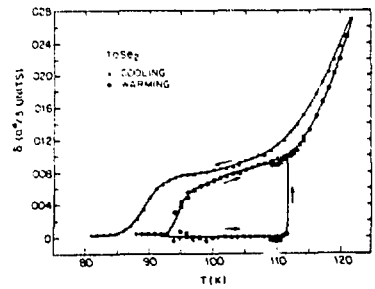


Fig. 1. Temperature dependence of incommensurability, $\delta$, in 2H-$TaSe_2$. On cooling only the fully incommensurate phase appears. On warming an additional stripe phase is present between $T_{cs}$=93K and $T_{si}$=112K. (After Fleming et al. (1980)).

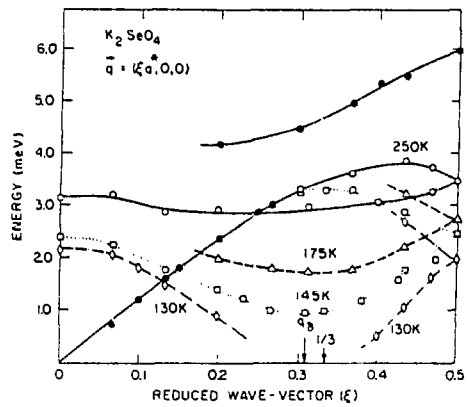


Fig. 2. Dispersion of the soft phonon branch in $K_2SeO_4$, leading to an incommensurate phase below $T_o$=130K. After Iizumi et al. (1977).

$T_o$ require new harmonic modes to be constructed from linear combinations of phonons with wavevectors $(\vec{q}+\vec{q}_o)$ and $(\vec{q}-\vec{q}_o)$ respectively. The result is an upper branch for which

$$\vec{u}_+(\vec{r},t) \sim \cos(\vec{q}\cdot\vec{r}-\phi)e^{i(\vec{q}\cdot\vec{r}-\omega_+ t)} \qquad (3)$$

and a lower branch for which

$$\vec{u}_-(\vec{r},t) \sim \sin(\vec{q}\cdot\vec{r}-\phi)e^{i(\vec{q}\cdot\vec{r}-\omega_- t)} \qquad (4)$$

Comparision of eqs. (2-4) shows that the upper branch is equivalent to a modulation of the amplitude of the static displacements, while the lower branch represents a modulation of their phase. Although phasons exhibit linear acoustic-like dispersion, $\omega(q)=vq$, the velocity v has no relation to the velocity of sound and the phasons are not to be confused with acoustic phonons, as Fig. 3 makes clear. It has proven difficult to unambiguously identify these phason modes with neutron scattering, but recently there have been reports of their observation in two incommensurate insulators, biphenyl (Cailleau et al. 1980) and $ThBr_4$ (Bernard et al. 1981).

The foregoing discussion concerned phason modes in displacive incommensurate structures. In intergrowth/overgrowth structures the phason does

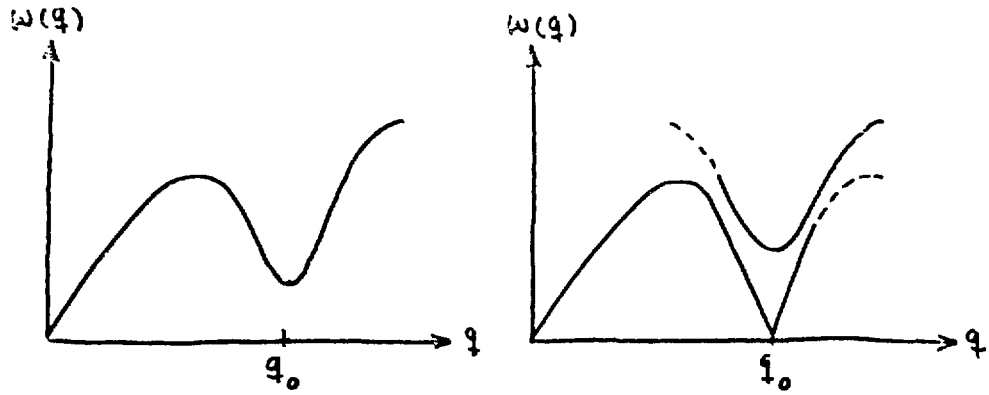


Fig. 3. Schematic illustration of the dispersion relation for a material undergoing an incommensurate displacive phase transformation. (a) soft branch with minimum at $q_0$ above $T_0$; (b) splitting of modes into a gapless 'phase' branch and an upper 'amplitude' branch below $T_0$.

represent (essentially) an acoustic mode of the sublattice. These modes have been studied extensively in $Hg_{3-\delta}AsF_6$ (Heilmann et al. 1979) and detailed discussions of their dispersion and damping have appeared recently (Axe et al. 1982).

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