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Incommensurate Structures

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Incommensurate structures

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A review is given of recent neutron scattering studies of displacive incommensurate structures, and the instabilities that occur within periodic crystalline structures that lead to their formation. The concept of a soft phonon, in some cases associated with an electronic screening anomaly, is useful but not always capable of a completely satisfactory description. An unusual one-dimensional liquid-like phase has been studied in the non-stoichiometric mercury compound $Hg_{3-\delta}AsF_6$.

Incommensurate structures

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

$$A(\boldsymbol{r}) = \sum_{\{\boldsymbol{G}\}} A_{\boldsymbol{G}}\, e^{i\boldsymbol{G}\cdot\boldsymbol{r}}; \quad B(\boldsymbol{r}) = \sum_{\{\boldsymbol{G}'\}} B_{\boldsymbol{G}'}\, e^{i\boldsymbol{G}\cdot\boldsymbol{r}}. \tag{1}$$

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

Magnetic and compositional modulation are well known and will not be considered further, although in both cases neutron studies have contributed greatly to our present understanding of these phenomena. I shall instead concentrate on the latter two cases, the first of which consists of interpenetrating (or overlaid) lattices of different spacing. In contrast to the first three cases, displacive modulation involves a periodic displacement, say

$$\boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{A}\cos(\boldsymbol{q}_0\cdot\boldsymbol{r} - \phi) \tag{2}$$

of the scattering centres away from an average position on a regular lattice site. It is not uncommon for the modulation amplitude, $\boldsymbol{A}$, to disappear above a certain temperature, the material thereby transforming from the incommensurate structure to a commensurate one with the average structure. This review is largely concerned with neutron scattering studies of such displacive incommensurate phase transformations, and of what they reveal of the nature of incommensurate instabilities. A final section is concerned with the unusual behaviour of the quasi-one-dimensional intergrowth compound, $Hg_{3-\delta}AsF_6$.

Soft mode instabilities and charge density waves

The form of (2) suggests that we view an incommensurate phase transformation as a condensation or 'freezing-in' of a phonon with wavevector $\boldsymbol{q}_0$, which might occur because the phonon frequency, $\omega^2(q_0)$, vanishes. Although introduced to explain ferroelectric ($\boldsymbol{q}_0 = 0$)

transformations (Cochran 1960) and subsequently generalized to include other high symmetry wave vectors on the Brillouin zone boundary (Cochran *et al.* 1968), there are no fundamental restrictions on the wavevector of a soft phonon instability.

TABLE 1

incommensurate structure type	$A(\boldsymbol{r})$	$B(\boldsymbol{r})$	example
1. magnetic	magnetic density, M	nuclear density, ρ	Cr, r.e. metals
2. compositional	average density, $\langle\rho_1+\rho_2\rangle$	differential density, $\langle\rho_1-\rho_2\rangle$	CuAu II, feldspars
3. intergrowth overgrowth	lattice ρ_1	lattice ρ_2	Ar on graphite $Hg_{3-\delta}AsF_6$
4. displacive	displacement field, $u(\boldsymbol{r})$	average density, $\langle\rho\rangle$	quasi-1 D and 2D metals, others

On a more microscopic level, such an incommensurate transformation may result from a charge density wave (c.d.w.) instability (Overhauser 1968) in the conduction electrons near the Fermi surface of a metal. The occurrence of such an electronic instability requires a large electronic susceptibility $\chi_0(\boldsymbol{q}_0)$, which is favoured when large portions of the Fermi surface are separated by the special wavevector $\boldsymbol{q}_0$. This favourable nesting of the Fermi surface is much more probable for quasi-one- or two-dimensional metals where the Fermi surface becomes independent of some components of electron momenta. The c.d.w. instability is coupled to the phonons because of the screening effect of the conduction electrons on the 'bare' phonon frequencies, $\Omega(\boldsymbol{q})$. In the random phase approximation, the observed physical phonon frequencies $\omega(\boldsymbol{q})$ are roughly of the form

$$\omega^2(\boldsymbol{q}) = \Omega^2(\boldsymbol{q})\left(\frac{1-\lambda_q^2\chi_0(\boldsymbol{q})}{1-v_q\chi_0(\boldsymbol{q})}\right),$$

where λ_q is an electron–phonon coupling constant and v_q is a Fourier component of the electron–electron interaction. Theory thus predicts the c.d.w. instability to be accompanied by a soft phonon $\omega(\boldsymbol{q}_0)\to 0$, where $\boldsymbol{q}_0$ is determined by the Fermi surface nesting. The phonon softening can be viewed as a giant Kohn anomaly (Kohn 1959). Neutrons scatter not directly from the c.d.w. but rather from the nuclear distortions resulting from the condensed phonon mode. (From a theoretical viewpoint, a mixed spin and charge density wave appears possible, but no spin components have yet been detected in c.d.ws.)

C.D.WS IN METALS

In quasi-one-dimensional metals, the Fermi surface approaches a set of parallel planes orientated perpendicular to the one-dimensional axis and separated by $2k_F$. This is the most geometrically favourable situation for c.d.ws with nesting occurring over the whole Fermi surface. It is often called a Peierls transformation, since Peierls (1955) first studied it in the mean field approximation long before physical manifestations were known.

The most striking confirmation of the existence of giant Kohn anomalies occurs in the quasi-one-dimensional conductor KCP ($K_2Pt(CN)_4Br_x$). This is well represented in figure 1, which shows neutron scattering data for longitudinal acoustic phonons propagating along $\boldsymbol{c}^*$, the one-dimensional Pt chain direction in this material (Carneiro *et al.* 1976). The anomaly is

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so sharply confined along $\boldsymbol{c}^*$ that a conventional representation in terms of a sharp phonon dispersion surface is not possible with experimental resolution. It is interesting to note that in spite of the unstable fluctuations shown in figure 1, it is now generally conceded that true incommensurate long-range order is not achieved in KCP, possibly because of the random potential from the non-stoichiometric ($x \approx 0.3$) Br ions. This is somewhat unfortunate, for this material is in other respects an example, *par excellence*, of Peierls's original idea.

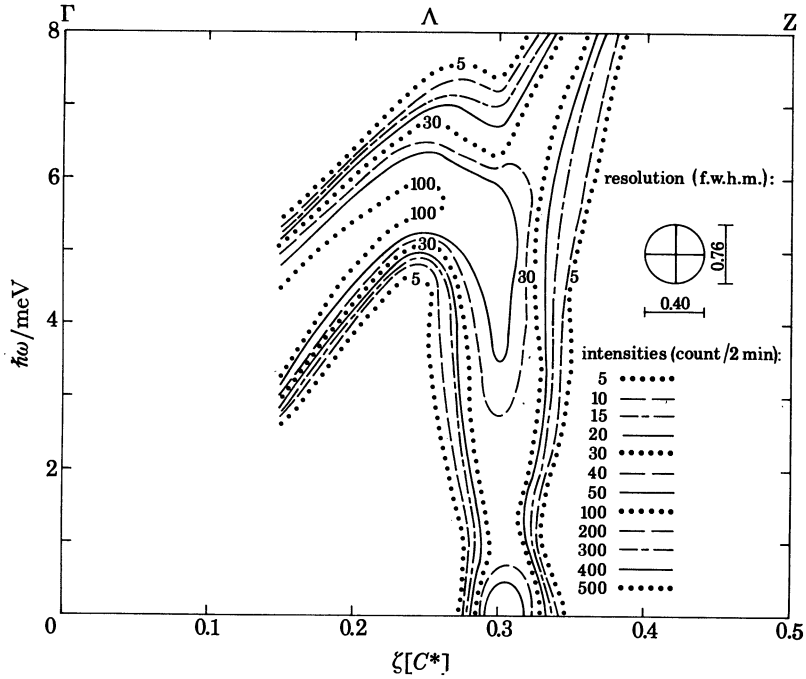

FIGURE 1. Intensity contours of inelastic scattering in KCP at 240 K showing extremely sharp Kohn anomaly near $\boldsymbol{q} = 0.3\,\boldsymbol{c}^*$. (After Carneiro *et al.* (1976).)

C.d.w. instabilities also occur in a number of quasi-two-dimensional transition metal chalcogenide compounds (Wilson *et al.* 1975). These materials have several different structural polytypes depending upon the stacking arrangement of the fundamental layers. I shall discuss only the 2H-polytypes of $NbSe_2$ and $TaSe_2$, for which the most extensive neutron studies are available. Unlike KCP, these substances undergo true phase transformations and their behaviour is at once more subtle and in some aspects better understood than is that of KCP.

Electron diffraction studies of both 2H-$NbSe_2$ and $TaSe_2$ showed satellite reflexions appearing at low temperature (Wilson *et al.* 1975). These peaks were originally thought to be commensurate with a spacing of one-third of the basal plane reciprocal lattice spacing $\boldsymbol{a}^*_{\mathrm{H}}$, but a subsequent neutron diffraction study (Moncton *et al.* 1975, 1977) showed that the ordering, which occurs at a well defined temperature, leads initially to incommensurate structures with wavevectors $\boldsymbol{q}_\delta = \frac{1}{3}(1-\delta)\,\boldsymbol{a}^*_{\mathrm{H}}$ with $\delta \approx 0.02$ at the transformation temperatures ($T_0 = 33.4$ and 122.3 K for $NbSe_2$ and $TaSe_2$, respectively). The temperature dependence of the satellite intensities, which is proportional to the square of the c.d.w. amplitude, is shown in figure 2. The transformations appear to be continuous (i.e. second-order) although it is impossible to rule out the possibility of a small first-order discontinuity.

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The most striking dynamical effect is a pronounced softening of the LA phonons propagating along a^*_H. As seen in figure 3, the wavevector minimum is very close to $\frac{1}{3}a^*_H$, as would be expected. This minimum is very insensitive to the c-axis component of momentum transfer, implying strong two-dimensional character. The square of the measured phonon frequencies at the minimum is plotted against temperature in figure 4. It is apparent that there is appreciable softening above T_0, and that this is reversed below T_0. It is also clear that the mode softening is far from complete at T_0, although the relatively poor experimental resolution may act to reduce the apparent sharpness of the anomaly. In addition to the inelastic scattering discussed above, there is also diffuse quasielastic critical scattering peaking near q_δ and at $T \approx T_0$.

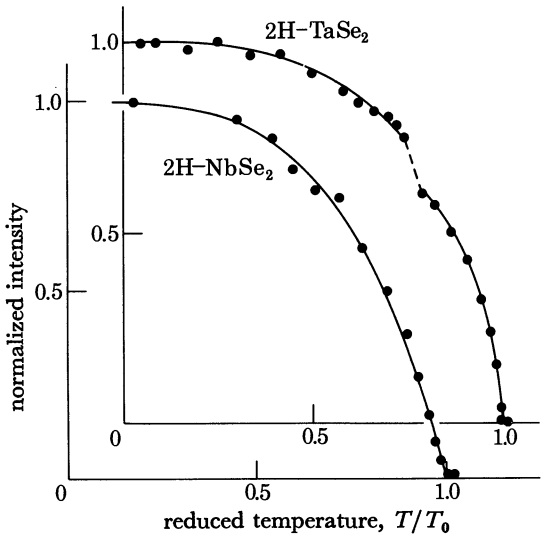

FIGURE 2. Temperature dependence of incommensurate satellite intensities in $TaSe_2$ and $NbSe_2$. (After Moncton *et al.* (1977).)

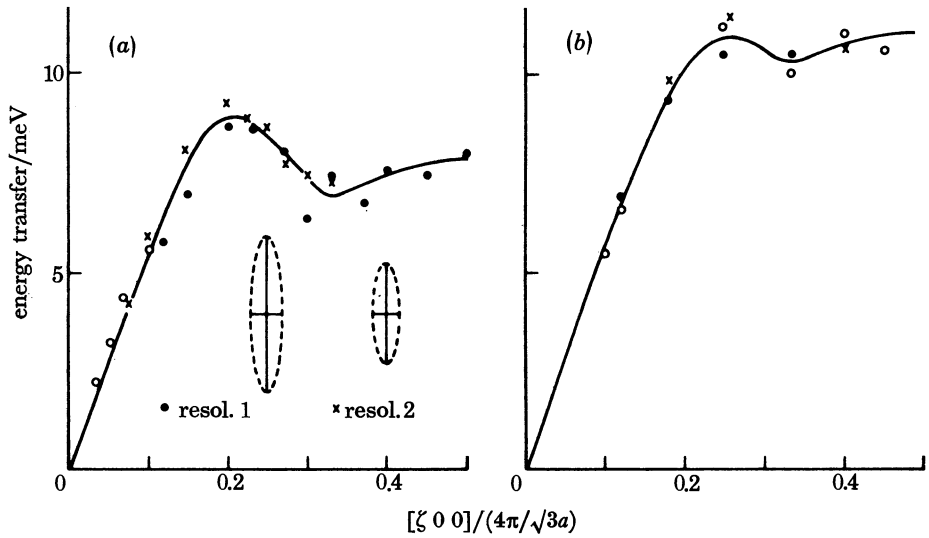

FIGURE 3. Phonon dispersion relations for Σ_1 phonon branches in $TaSe_2$ (a) and $NbSe_2$, (b) at 300 K. (After Moncton *et al.* (1977).)

An example of a nearly one-dimensional metal that does undergo a true c.d.w. transformation is afforded by TTF-TCNQ, an organic salt composed of tetrathiofulvalene (TTF^+) cations and tetracyanoquinodimethane ($TCNQ^-$) anions. Both are planar aromatic molecules that stack, plate-like, with overlapping partly filled π-orbitals responsible for the electronic conductivity. Incommensurate displacive modulations appear below $T_0 = 54$ K with a wavevector component along the stacking direction determined by the 1D Fermi surface, $2k_F = 0.295\, b^*$.

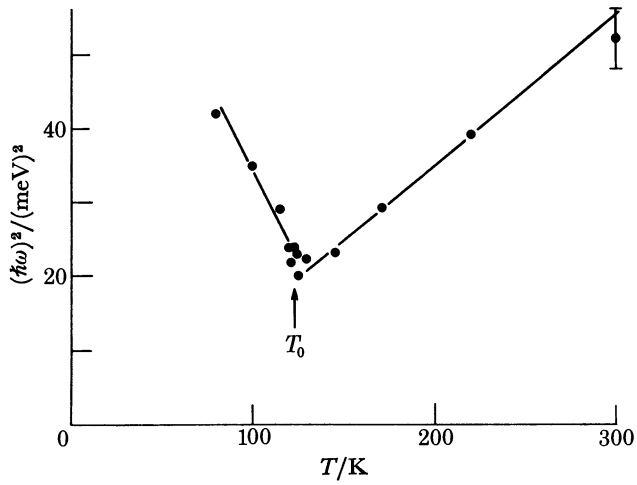

FIGURE 4. Temperature dependence of soft phonon energy in $TaSe_2$. T_0 marks the onset of c.d.w. formation. (After Moncton *et al.* (1977).)

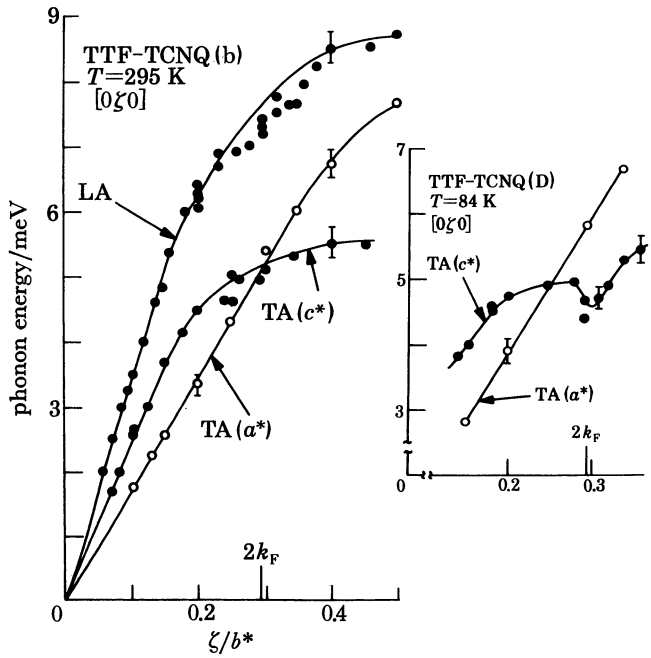

FIGURE 5. Dispersion of acoustic phonons propagating along b^* in TTF–TCNQ. (After Shapiro *et al.* (1977).)

Diffuse planes of strongly temperature-dependent X-ray scattering are observed below *ca.* 150 K, with the wavevector $2\boldsymbol{k}_F = 0.295\, b^*$. Atomic displacements with components along both $\boldsymbol{b}^*$ (longitudinal) and $\boldsymbol{c}^*$ are observed. The inelastic neutron scattering data on deuterated samples (Shirane *et al.* 1976; Shapiro *et al.* 1977; Mook *et al.* 1977) show a distinct (but rather weak compared with KCP) dip in the TA branch with (mostly) c^*-axis polarization (see figure 5). At the minimum, the phonon energy decreases somewhat with decreasing temperature, but appears to remain more than 4 meV. If there is any anomalous dip in the LA branch at $2\boldsymbol{k}_F$, it is considerably weaker than for TA(c^*), and the energies increase with increasing temperature. There is likewise no evidence for anomalies in the remaining TA(a^*) mode.

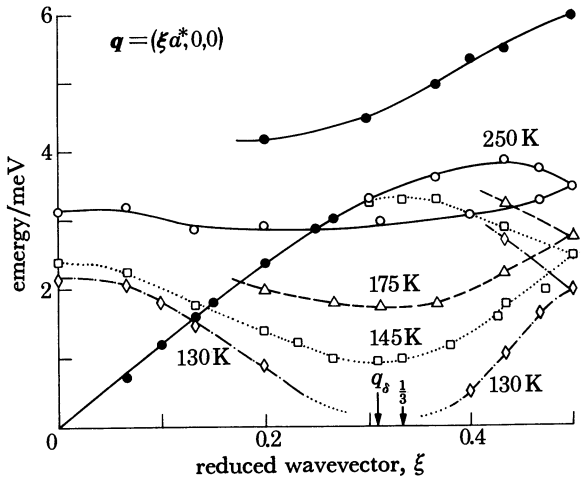

FIGURE 6. Dispersion of Σ_2, Σ_3 soft mode branch of K_2SeO_4 in an extended zone scheme. (After Iizumi *et al.* (1977).)

INSULATORS

In low dimensional metals the forces responsible for the instability are due to ion–electron–ion interaction and are long-ranged and oscillatory. The result, as we have seen, can be a sharp anomaly about $\boldsymbol{q}_0 = 2\boldsymbol{k}_F$. In insulators studied so far, the effective interaction ranges are shorter, leading to broader phonon anomalies, which are very conveniently studied by inelastic neutron scattering. In insulators, there is no essential requirement for incommensurate instabilities which favours low spatial dimensionalities, and indeed the known examples lack any obvious lower pseudo-dimensionality.

The most detailed neutron scattering study to date has been performed on K_2SeO_4 (Iizumi *et al.* 1977), which undergoes an incommensurate transformation at $T_0 = 130$ K. Figure 6 shows the dispersion of the soft phonon branch as a function of temperature. It is somewhat perverse that whereas all of the c.d.w. transformations in metals studied thus far do not follow the prediction of a simple soft mode instability, $\omega \to 0$ at $T = T_0$, such behaviour is seen in K_2SeO_4 for which no comparably simple and elegant microscopic description presents itself. On a phenomenological level, however, we can use the observed shape of dispersion relations such as that shown in figure 6 to deduce something about the effective force constants that couple planes of atoms perpendicular to the propagation direction. We find that from this point of view, the instability in K_2SeO_4 is brought about by an anomalously large force constant between planes of atoms which are third-nearest neighbours.

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'Lock-in' transformations

We have seen that incommensurate structures arise from a competition of forces of varying range. However, even in the incommensurate state there are interactions at work which tend to restore periodicity. The ways in which these forces manifest themselves are illustrated in figure 7, which shows the temperature dependence of the wavevector of the incommensurate satellites in the transition metal dichalcogenides $NbSe_2$ and $TaSe_2$. The most striking feature is the abrupt change of the satellite vector in $TaSe_2$ from $\boldsymbol{q}_1 = \frac{1}{3}(1-\delta)\,\boldsymbol{a}_1^*$ to the commensurate value $\frac{1}{3}\boldsymbol{a}_1^*$, which occurs at $T \approx 0.76\,T_0$. $NbSe_2$ does not achieve the $\frac{1}{3}\boldsymbol{a}_1^*$ commensurate state even at the lowest attainable temperatures, but as in $TaSe_2$ the satellite wavevector shows a pronounced temperature dependence, whose origin is closely related to the 'lock-in' phenomenon itself.

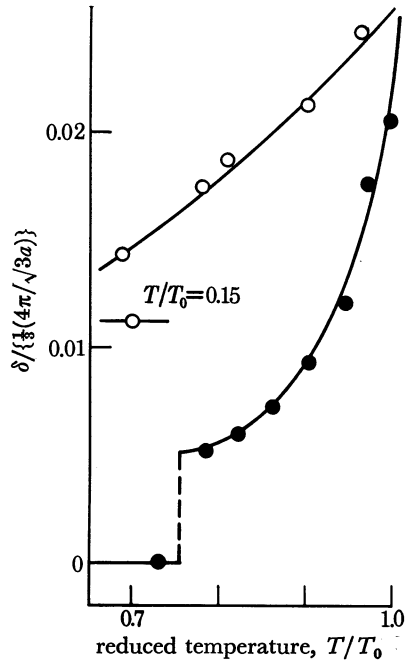

Figure 7. Temperature dependence of the satellite wavevector $\boldsymbol{q}_\delta = \frac{1}{3}(1-\delta)\,\boldsymbol{a}^*$ in $TaSe_2$ (●) and $NbSe_2$ (○). (After Moncton *et al.* (1977).)

Similar lock-in transformations have also been observed in other incommensurate systems. It would be inappropriate to present an extended discussion of these interesting transformations here, although neutron scattering observations were responsible both for their discovery and initial elucidation (Moncton *et al.* 1977). The key point is to recognize that purely sinusoidal modulation (equation (2) with ϕ constant) cannot take advantage of the periodic potential of the average lattice. The regions where the displacements are in phase with the potential are exactly cancelled by equally large and numerous out-of-phase regions. However, with the proper spatial variation of $\phi(\boldsymbol{r})$ the in-phase regions grow at the expense of the out-of-phase regions, thus lowering the total energy. A careful analysis of this effect (McMillan 1976) shows that this also produces a gradual pulling of the wavevector $\boldsymbol{q}_0$ away from its initial (zero amplitude) value toward one commensurate with that of the average lattice. This phase

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modulation also produces additional secondary satellite reflexions that are initially weak but which grow to intensities comparable to the primary satellites near lock-in. Such behaviour has been observed in $TaSe_2$.

Phasons

What happens if we extend the soft mode picture of the phonons just above T_0 to discuss the lattice dynamics of the incommensurate state? A simple analysis assuming purely sinusoidal static displacements (McMillan 1975; Axe 1976) produces results shown schematically in figure 8. Above T_0, there is a soft branch with a minimum frequency $\omega(\boldsymbol{q}_0) \to 0$ as $T \to T_0$.

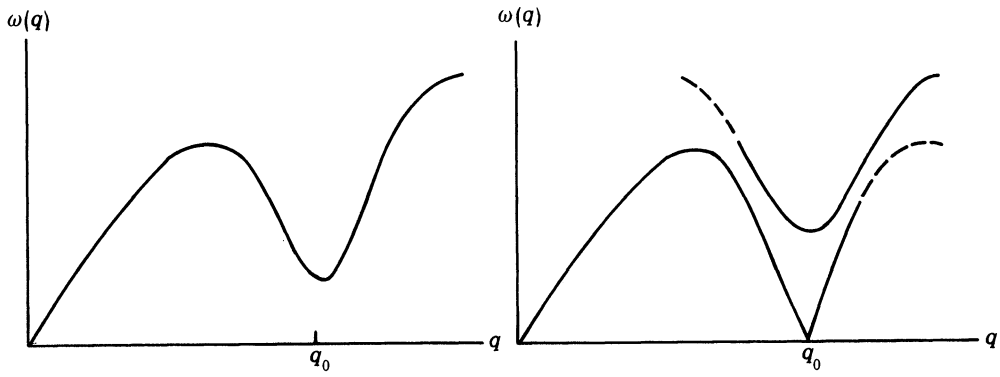

Figure 8. Schematic illustration of the dispersion relation for a material undergoing an incommensurate displacive phase transformation: (*a*) above T_0 there is a soft branch with a minimum at q_0; (*b*) below T_0 there is a 'splitting' of the modes into a gapless 'phase' branch and an upper 'amplitude' branch.

Below T_0 the added presence of the static displacements require new harmonic modes to be constructed from linear combinations of phonon wavevectors $(\boldsymbol{q}+\boldsymbol{q}_0)$ and $(\boldsymbol{q}-\boldsymbol{q}_0)$ respectively. This results in a splitting of the modes into an upper 'branch' for which

$$u_+(\boldsymbol{r}, t) \approx \cos(\boldsymbol{q}_0 \cdot l - \phi)\, e^{i(\boldsymbol{q}\cdot\boldsymbol{r} - \omega_+ t)} \tag{3}$$

and a lower 'branch' for which

$$u_-(\boldsymbol{r}, t) \approx \sin(\boldsymbol{q}_0 \cdot \boldsymbol{r} - \phi)\, e^{i(\boldsymbol{q}\cdot\boldsymbol{r} - \omega_- t)} \tag{4}$$

Comparison of (2)–(4) shows that for small q the upper branch is equivalent to a time-dependent modulation of the *amplitude* of the static displacements, whereas the lower branch represents a modulation of their *phase*. Inevitably, the term 'phason' has become accepted nomenclature for these latter modes, which are gapless and exhibit linear acoustic-like dispersion, $\omega_-(q) = vq$. However, the velocity v has no relation to the velocity of sound and the phasons are not to be confused with acoustic phonons, as figure 8 makes clear.

Of course, I have already pointed out that the static displacements are in general more complex than (2) suggests. Furthermore, we have seen that incomplete phonon softening renders the whole soft mode picture of little more than qualitative value in many cases. Nevertheless, we know on more general grounds that the absolute phase of the static distortion is not fixed by energetic considerations in an incommensurate structure and this fact alone guarantees a gapless phason branch. (Technically, phasons are Goldstone modes associated with a broken continuous symmetry. Only a pinning of the overall phase of the static distortion by lock-in terms or impurities will cause a gap to appear in the phason spectrum.) Fröhlich (1954)

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first recognized the unusual character of these excitations and used them to construct a novel and as yet unobserved mechanism for superconductivity.

In view of the unusual nature of phason excitations, the possibility that they make interesting contributions to various thermal and transport properties and the fact that inelastic neutron scattering seems ideally suited to their study, it is curious (and somewhat disconcerting) to note how little has in fact been learned, through no lack of effort. In fact, I am currently unaware of any *convincing* direct evidence for the existence of low-frequency propagating phason modes in any of the displacive incommensurate phases so far studied, although there is commonly observed unresolved additional scattering, which may represent *very* low frequency propagating and/or overdamped excitations. Fresh experiments and ideas are needed.

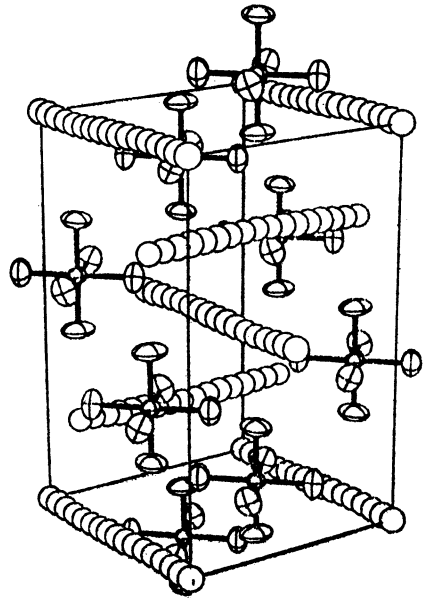

FIGURE 9. The structure of $Hg_{3-\delta}AsF_6$. (After Shultz *et al.* (1978).)

$Hg_{3-\delta}AsF_6$: A ONE-DIMENSIONAL LIQUID

This remarkable material, whose structure is shown in figure 9 consists of a tetragonal AsF_6 lattice in which there are open non-intersecting channels running parallel to both basal plane edges. These channels are filled with tightly packed chains of Hg ions. The observed interchain Hg–Hg distance is such that $3-\delta$ ($\delta \approx 0.18$) Hg ions can be accommodated within a unit cell dimension of the AsF_6 lattice (Schultz *et al.* 1978). The low-temperature diffraction pattern consists of two distinct series of Bragg reflexions from separate, well ordered and incommensurate sublattices. The material is thus an example of an incommensurate structure of the intergrowth type (table 1). (In these materials, the Goldstone phason modes *are* independent acoustic phonons propagating on their respective sublattices and they *have* been directly observed by neutron scattering (Hastings *et al.* 1977; Heilmann *et al.* (1978)).

Above 120 K, the Bragg peaks of the Hg lattice disappear, to be replaced by a series of narrow sheets of scattering perpendicular to and spaced at a regular interval along the Hg chain axes. Such a one-dimensional diffraction pattern shows that the position along the chain

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of an arbitrarily chosen origin Hg ion is no longer fixed either with respect to the AsF_6 lattice or with respect to neighbouring Hg chains. Although the sheets of scattering were initially thought of as elastic 'Bragg sheets', this notion violates very general theorems that show the impossibility of true long-range periodic order in one dimension. Emery & Axe (1978) analysed the behaviour of a one-dimensional chain of atoms bound by harmonic nearest neighbour forces. In this model, sheets of scattering have a typically liquid-like diffraction pattern, as shown in figure 10, although in this figure the parameter σ/d, which characterizes the mean square thermal fluctuations relative to the mean near-neighbour spacing, d, is for illustrative purposes chosen to be considerably larger than is appropriate for $Hg_{3-\delta}AsF_6$($\sigma/d \approx 2.5 \times 10^{-2}$ at 300 K.)

For small (σ/d) the peak profiles are predicted to be Lorentzian, the width of successive peaks, $n = 1, 2, \ldots$, being proportional to n^2, the proportionality constant expressible in terms

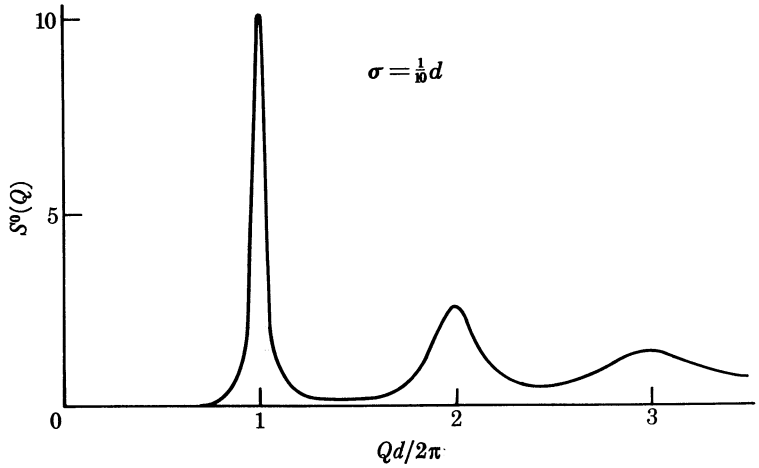

FIGURE 10. The diffraction pattern of a one-dimensional harmonic liquid. For small σ/d the width of successive peaks is proportional to n^2.

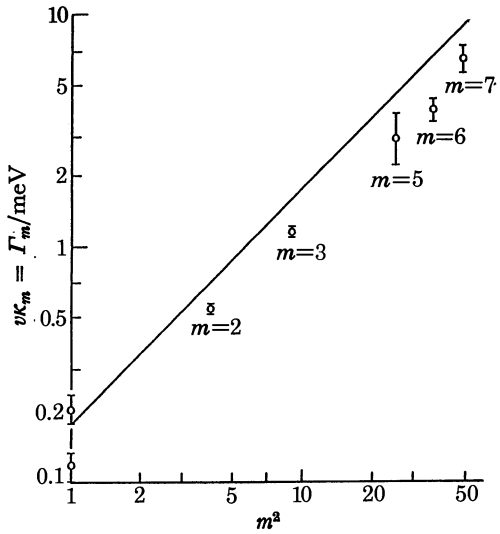

FIGURE 11. A comparison of experimental and theoretical values of the successive peak widths in $Hg_{3-\delta}AsF_6$ at 300 K. (After Heilmann *et al.* (1979).)

of the velocity of sound along the chain, v_1. Experiments measuring the width of successive sheets up to $n = 7$ were subsequently performed (Heilmann *et al.* 1979). The results, shown in figure 11, not only confirm the predicted n^2 dependence, but the value of v_1 derived from the measured widths is within 20 % of the directly measured values (Heilmann *et al.* 1978). Thus the Hg chains do, at high temperature, behave like independent columns of one-dimensional harmonic liquid.

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