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# INCOMMENSURATE CRYSTALS:

## A New Phase in Solid State Physics

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| **Type** | **Examples** |
|---|---|
| Ionic crystals | $Na_2CO_3$, $K_2SeO_4$, $Rb_2ZnBr_4$, $ThBr_4$ |
| Metals | CuAuII, $MgSi_{2-x}$ |
| Semiconductors | $TaS_2$, $TaSe_2$, $NbSe_2$ |
| Organic | TTF-TCNQ, Biphenyl, Thiourea |
| Organo-metallic | KCP |
| Magnetic | Cr, Er, Tm |
| Minerals | Plagioclase, $\beta$-eukryptite, Quartz |
| Ferroelectric | $NaNO_2$ |
| Intergrowth | $Hg_{3-x}AsF_6$, $TTF_7I_{5-x}$, $Eu_{1-x}Cr_2Se_{4-x}$ |

In the 18th century the morphology of crystals was explained by the hypothesis that crystals consist of elementary blocks repeated in all three space directions. This was confirmed experimentally by von Laue, who showed that the diffraction peaks in X-ray scattering are associated with the points of a lattice. Since then, the prevailing idea in solid state physics has been that essentially, a crystal has lattice translation symmetry, at least if one neglects local defects and disregards finiteness.

During the 1960s however, careful analysis of the diffraction pattern of several compounds (some of them very common like anhydrous soda at room temperature, $\gamma$-$Na_2Co_3$) showed that these materials have a long range order comparable to that of other crystals (this follows from the sharpness of the peaks) but not a lattice translation symmetry. The structure can be described as follows: starting from a basic structure, which describes a kind of average structure where the atom positions do have lattice translation symmetry, these are displaced in the real crystal (up to and over 0.5 Å). Moreover, and this is characteristic, the displacements are spatially periodic and, usually, have the same period for different atoms in the unit cell. They constitute what is called a modulation wave.

Hence in the simplest case there are four elementary periodicities involved: three pertaining to the lattice of the basic structure and one to the modulation wave. One can see this from the diffraction pattern: next to the main reflections of the basic structure there are satellite reflections, whose distance to the nearest main reflection is inversely proportional to the period of the modulation displacements (Fig. 1).

If the period of the modulation is rationally dependent on the other three, the crystal still possesses lattice translation symmetry. In this case, which occurs frequently, one can reduce to three the number of independent periodicities and the modulated crystal is said to form a *superstructure* of the undistorted phase.

In contrast to that situation, the characteristic typical of the new crystal phases, like $\gamma$-$Na_2CO_3$, is that the period of the modulation varies (as a function of temperature) independently of the variation of the

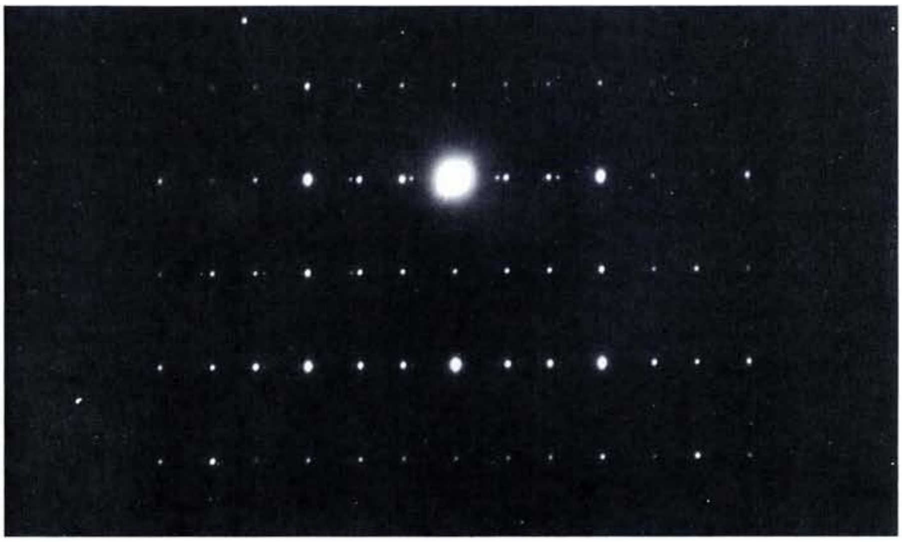

*Fig. 1 — Electron diffraction pattern of $Rb_2ZnBr_4$.*

### Contents

Incommensurate Crystals 1
Surface Science 5
Solar & Stellar Magnetic Fields 6
Boundary and Interior Layers 6
Progress in Refrigeration to Ultralow Temperatures 7
Polymer Crystals: Structure and Morphology 10
New Members of EPS 10
Closing the EPS Ranks 11
National Societies 11
Divisional News 12
Official Announcement 12

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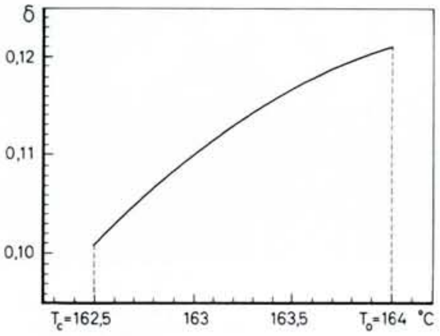


*Fig. 2 — Temperature dependence of the wave vector of the modulation of $NaNO_2$ (D. Durand et al., Ref. 2).*

basic lattice distances (Fig. 2). So in general, the 4th period is incommensurate with the other three. This explains the name "incommensurate" crystal phase. Clearly such a phase cannot have lattice translation symmetry, at least not in three dimensions.

Even before the investigation of soda, one had found incommensurate periodic orderings in crystals, for instance, ordering of spins in magnetic systems. The magnetic structure may be complex, but it still leaves the atoms at their ideal crystallographic positions (at least within a reasonable approximation). In soda, the situation is fundamentally different, as the complexity observed occurs at the level of the geometrical crystal structure.

Since the discovery of this phenomenon, a very large number of other incommensurate crystal structures have been found. The phenomenon is not restricted to a particular type of compound and appears to occur quite generally (see Table).

Roughly speaking, one can distinguish several types of incommensurate crystal structure (Fig. 3). One can be described by a displacement wave as discussed above, and it is called a *displacive modulation*. In another, the occupation probability of a site by an atomic species has a periodic character — *occupation modulation*, and finally a crystal may consist of two or more subsystems, with their own lattice periodicities, which are mutually incommensurate. Such a crystal is called incommensurate *intergrowth* (or *composite*) *structure*. A combination of these different types may also occur.

### Examples and Characteristic Properties

A well studied example of a compound with an incommensurate crystal phase is potassium selenate ($K_2SeO_4$), which above $T_i$ = 128 K has a normal crystal structure. If the temperature is lowered towards $T_i$ however, one branch of the phonon spectrum develops a minimum of increasing depth for a wave vector $\vec{q}$ at a general position inside the Brillouin zone and, at $T = T_i$, the frequency of the corresponding mode (a so-called soft mode) goes to zero. This means that at that temperature, the crystal is unstable. The stable structure for $T < T_i$ is an incommensurate crystal phase of the displacive type with the same modulation wave vector $\vec{q}$ as that of the original soft mode.

If the temperature is lowered still further, another phase transition takes place at $T_c$ = 93 K yielding again a normal crystal, but with one of the lattice periodicities three times as large as it was above $T_i$. One thus gets a 3-fold superstructure of the high temperature phase. The phase transition at $T_c$ is called a *lock-in transition*.

As for any thermodynamical phase, the incommensurate crystal phases are stable within a certain temperature range. This range may be of the order of hundreds of degrees (e.g. in $Na_2CO_3$) or a few degrees (e.g. 1 deg in $NaNO_2$). There are also crystals for which no lock-in transition has been found, even at very low temperatures.

Incommensurability is observed in intergrowth crystals as well. For example in $(TTF)_7I_{5-x}$ the TTF molecules form a crystal structure which has large channels built in. In these channels one finds chains of iodine atoms which, at room temperature, are crystallographically ordered also. Because the lattice constant of the iodine substructure in the chain direction is incommensurate with that of the TTF substructure, there is no common lattice translation symmetry. Such an incommensurate composite structure can also occur in layered compounds. Similarly, atoms adsorbed at the surface of a crystal give rise to a (two-dimensional) incommensurate intergrowth pattern if the adsorbed atoms order and their lattice constants do not fit those of the substrate.

An extensively studied class of incommensurate crystal phases is that of quasi-one (or -two) dimensional conductors. If the coupling between electrons and lattice is strong enough, a new equilibrium state is formed where in the ground state, the conduction electrons do not have a spatially uniform distribution (in the free electron approximation), but one that is modulated owing to the presence of charge density waves (CDW). The underlying lattice then gets distorted by a modulation tracking the CDW. Examples are found among dichalcogenides ($TaS_2$, $TaSe_2$) where also there can be two additional elementary periodicities. This is expressed by the term two-dimensional modulation.

In principle, the number of additional periodicities can be arbitrarily large, but the dimensionality of the modulation of the most complex case known so far is three ($FeO_{1-x}$). One can show that if the modulation arises from soft modes at $q$ vectors from one "star" (vectors obtained from a single vector using point group symmetry) the number of additional periodicities is at most nine.

### Origin of the Phenomenon

For some of the systems mentioned above, notably those involving charge density waves, the origin of the incommensurate phase is fairly well understood. Peierls a long time ago showed that a one-dimensional crystal with conduction electrons is unstable against a deformation with a wave vector which is twice the Fermi wave vector.

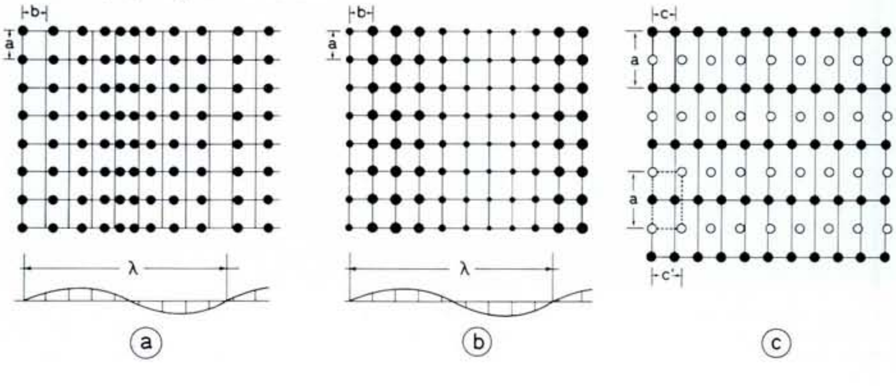
Although strictly speaking no one-dimensional crystals exist in nature, there are many quasi-one-dimensional conductors, with significant conductivity along one direction only (see M. Weger, *Europhysics News,* **9**, 7/8, p. 7). One then observes the appearance of CDW and of displacive modulation exactly as predicted theoretically.

Depending on the shape of the Fermi surface, a similar instability can also occur in quasi-two-dimensional conductors, as indeed observed in systems like $TaSe_2$. Since, in general, the Fermi wave vector is incommensurate with the reciprocal lattice vectors of the (average) crystal structure, the resulting deformation is incommensurate.

Also if there are two or more subsystems, each with its own lattice periodicity, the overall result will be an incommensurate phase, with modulations produced by the mutual interaction between the subsystems.

Sometimes, the appearance of different elementary periodicities can be understood by considering e.g. the radii of the atoms involved, but not always. In particular, in ionic modulated crystals, the intrinsic mechanism leading to incommensurability is little known. A clue may lie in the

*Fig. 3 — Three forms of incommensurate crystal phases: a) displacive modulation; b) occupation modulation; c) composite structure.*



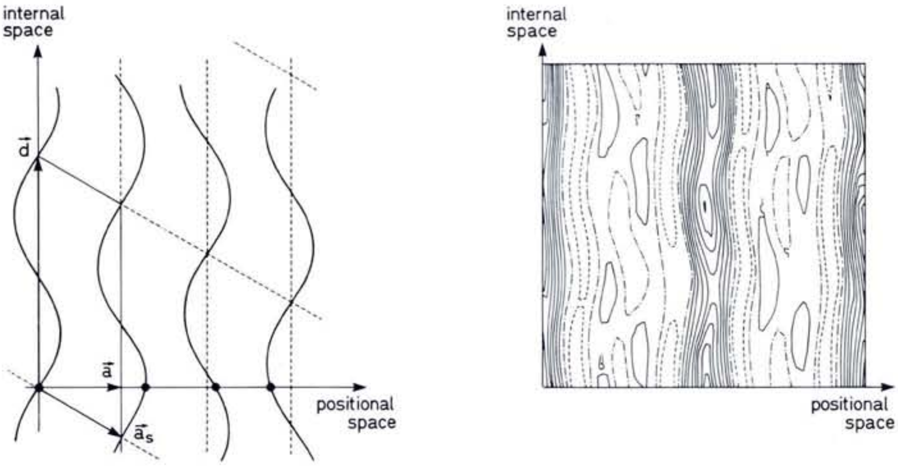


*Fig. 4 — Supercrystal in two dimensions corresponding to a one-dimensional modulated crystal. On the r.h.s. electron density in $Fe_{1-x}S$ plotted in superspace (Nakazawa et al., AIP Conf. Proc.* 53 *(1979) 358).*

behaviour of one-dimensional models, where it has been shown that competitive harmonic forces, in combination with anharmonic interactions, can give rise to incommensurate crystal phases. In ionic crystals, similar competitive forces arising from the Coulomb interaction, may be the cause of incommensurability.

### Symmetry

Because of the presence of four (or more) elementary periodicities in space (which is three-dimensional), the incommensurate crystal does *not* have a *lattice translation symmetry*. Nevertheless it is possible to recover a lattice structure as follows.

If $\vec{n} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
describes the position of a unit cell,
$\vec{r}_j$ the average position of the $j$ th atom in the unit cell and
the displacement of the atom at $\vec{n} + \vec{r}_j$ is $\vec{u}_j(qn + t)$ (where $\vec{u}_j(x)$ is periodic:
$\vec{u}_j(x) = \vec{u}_j(x + 2\pi)$),
the phase $t$ of the modulation wave can be interpreted as a new free variable. Then one can write the atomic positions as points in a (3 + 1)-dimensional space, the coordinates $(\vec{r}, t)$ of which become:

$$(\vec{n} + \vec{r}_j + \vec{u}_j(qn + t), t)$$

For fixed $\vec{n}$ and $j$ this represents a line in a 4-dimensional space (Fig. 4). Moreover, the pattern of all lines has 4-dimensional lattice translation symmetry: it is left invariant by the translation $(\vec{m} = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3, -qm)$ and $(0, 2\pi)$, where $m_1, m_2$ and $m_3$ are integers. The actual crystal is obtained as a section $t = 0$ of these lines with the 3-dimensional space. The lattice translation symmetry obtains its relevance from the fact that the projection of the Fourier components of the 4-dimensional structure on the 3-dimensional space gives the Fourier components of the incommensurate crystal, and this projection is one to one.

The incommensurate crystal has thus a well-defined correspondence with a structure having lattice periodicity, although defined in a 4-dimensional space, rather than in real space. The symmetry group of the 4-dimensional pattern is taken as the symmetry of the incommensurate crystal.

The first application of this approach is that one can *classify* the possible symmetry groups of incommensurate crystal phases and assign one to any such structure. We have developed systematics for determining them, and have produced a list of all inequivalent 4-dimensional "superspace groups" as well as a list of all Bravais lattice types up to the sixth dimension. In this classification, the normal 3-dimensional structure appears as a special case, so that as well as having an extended classification we also get a unified description. Determination of the superspace group is possible, and has indeed been performed for several compounds along the same lines as that of an ordinary space group for a normal crystal.

A second application is important for crystal structure determination. Owing to the fact that there is such a close relationship between the Fourier coefficients of a real crystal and those of the corresponding 4-dimensional structure (the *supercrystal*), it follows that if there are systematic extinctions in the latter as a consequence of the superspace symmetry relations, the same systematic extinctions are also present in the diffraction pattern of the real crystal. This is of great help in structure analysis, since the restrictions imposed on the supercrystal by symmetry lead to structural relations in the real crystal.

Finally, the higher dimensional symmetry groups may be applied to the physics of incommensurate crystal phases, analogous to the application of 3-dimensional space groups to ordinary crystals. In particular, excitations may be labelled with vectors in a 4-dimensional Brillouin zone, although there is no Brillouin zone for such structures in three dimensions. In this way, one of the most powerful techniques in solid state physics, the application of group theory, may be brought into play.

### Physical Properties

Most of the properties of amorphous materials differ only slightly from those of regular crystals. The same is true *a fortiori* for incommensurate crystal phases; only a careful analysis reveals the subtle differences. We shall discuss here some of the new features.

Already in the *macroscopic form* of a crystal one can see the regularity of the microscopic structure as normally, the crystal faces relate to net-planes of the crystallographic lattice. If one chooses suitable axes, they intersect the net-planes at points for which the ratios of the distances to the origin are rational, as expressed by the *law of rational indices*. Departures from this law can be expected when a crystal does not have lattice periodicity, as in the case of an incommensurate crystal structure. Indeed such departures have now been found, and the experimental evidence is compatible with the view that the 3-dimensional form of a crystal is the real space intersection of a supercrystal which has a form in agreement with the generalization to higher dimensions of the law. In practice this means that there are additional crystal faces and these can be labelled by four (or more) integers (the new Miller indices).

On the microscopic level, one has to determine the modulation functions $\vec{u}_j$

which so far, has been done for very few cases only. Nevertheless, both experiment and theory lead to the following picture. Just below the phase transition temperature $T_i$ the modulation has a simple (sinusoidal) form, but if the temperature is lowered, higher harmonics come in. Near the lock-in transition, the structure should be described in terms of small domains having a nearly commensurate structure, separated by walls, where the modulation function changes rapidly. These walls are called *discommensurations* (and sometimes phase solitons). It is possible that the wave-vector of the modulation, i.e. the average over commensurate domains and discommensurations, is commensurate in this region: if the temperature changes the wave vector jumps from one commensurate value to another.

The *lattice vibration spectrum* of an incommensurate crystal is very different from that of an ordinary crystal. If one has an *m*-fold superstructure, the Brillouin zone shrinks by a factor *m* and at the new zone boundaries, gaps are created. In an incommensurate phase there is no 3-dimensional Brillouin zone left and there is an infinite number of gaps. Numerical calculations performed on simple models, however, show that the width of these gaps varies strongly. If the modulation does not contain many higher harmonics, there are only a small number of important gaps, the others are very small, and can be neglected in practice. Furthermore since the vibrations with wave vector $\vec{k} = 0$ can be optically active, and the number of such modes is infinite, there are in principle an infinite number of new lines in the spectra. In practice, however, again only a small number of new active modes appear at the phase transition from the normal to the incommensurate phase. This feature has already found experimental verification in infrared absorption and Raman scattering spectra.

There are also qualitatively new excitations in incommensurate phases. These can be described as long wavelength fluctuations in phase or amplitude of the modulation function. They are called, therefore, *phasons* and *amplitudons*. If the modulation function is smooth and the modulation wave vector incommensurate, one expects the phasons to have zero frequency. Although in superspace one can view a phason as an acoustic mode with displacements in the additional space direction, it has proved extremely difficult to find such phason branches experimentally. Only in biphenyl and in $ThBr_4$ have they been reported (from direct measurements by inelastic neutron scattering). On the other hand, relaxation time measurements using NMR show that there are new low-lying excitations which are interpreted as phasons. Work to detect phasons optically is in progress.

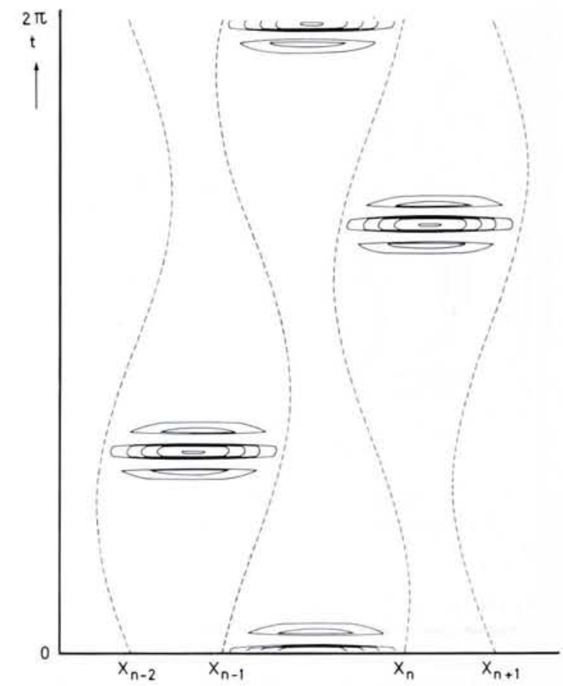


*Fig. 5 — Electron density in a supercrystal corresponding to a one-dimensional modulated crystal for a localized state (C. de Lange, T. Janssen, to appear).*

The *spectra of electrons* in incommensurate crystal phases show a large number of gaps as well. Here also there is a hierarchy in the spectrum: there are a few broad gaps, but in between, within each resulting pseudo-band, there are smaller and smaller gaps, which become less and less important, because an electron can jump over small gaps under the influence of thermal excitations or small electric fields.

An interesting phenomenon is that of the localization of electronic states. In ordinary crystals, all eigenstates are extended over the whole crystal. In one-dimensional amorphous systems, all eigenstates are localized. Model calculations show that in one-dimensional incommensurate crystal phases, both extended and localized states occur; presumably this will be the case in 3-dimensional incommensurate crystals as well. Strictly, localized eigenstates are restricted to a finite region in the crystal and correspond to discrete energy eigenvalues, but extended states occur for eigenvalues appearing in energy bands. In addition there are states which are periodic, and thus extend through the whole crystal. These are characterized by the presence of maxima separated by regions of very low probability. The peculiar character of localized states in a modulated crystal appears more clearly if one plots these states in superspace together with the atomic modulation lines (Fig. 5).

## Theoretical Considerations

Once the existence of incommensurate crystal phases had been firmly established, the investigation of these materials became a joint effort of experimentalists and theoreticians, most of the work being devoted to charge density wave systems which are fairly well understood by now.

Phase transitions were, in the first place, studied using Landau theory (Ishibashi, Levanyuk & Sannikov, Bruce & Cowley) taking as order parameter, the average value of the normal coordinate corresponding to the soft mode. Fluctuations in the order parameter are identified with lattice vibrations. Near the lock-in transition, it has been shown by McMillan that discommensurations can be formed. Symmetry arguments based on the basic structure play an important role here (J.C. and P. Toledano).

Incommensurate ionic crystals and semiconductors were first studied using models for intergrowth structures or incommensurate surface phases, that suggested by Dehlinger in 1927 being given greatest attention. Later Frenkel and Kontorova, Frank and Van der Merwe, Ying, Aubry and Bak examined this one-dimensional model for a harmonic chain in a periodic background potential.

Models for incommensurate crystal phases of intrinsic origin have been studied from the lattice dynamical point of view (Haque and Hardy), and others (Bilz and Buettner, Janssen and Tjon, Parlinsky and Michel) where competitive forces and anharmonic terms are taken into account. In a molecular field approximation, the phase diagram for such a model can be determined, which shows that for sufficiently strong 3rd neighbour interactions, there is a soft mode with a wave-vector at a general point of the Brillouin zone, and a stable ground state corresponding to an incommensurate crystal phase which is intermediate between an ordinary crystal and a superstructure. Moreover, it shows the existence of low-frequency phasons near the incommensurate phase transition temperature and discommensurations near the lock-in transition.

### Conclusion

Incommensurate crystal phases show a wealth of detail which are, however, not always easy to disentangle. From the physical point of view, the causes of the stability of these phases are more or less understood, although there are still many questions outstanding, partially of a technical, but also of a fundamental nature. For small deviations from normal periodicity, perturbative schemes are useful, but in general, the non-linear effects are too big for such approximations to be applicable. The better approach would seem to lie in an extension of the usual solid state theory in a way that makes use of the crystallographic superspace symmetry group. One has then, of course, to interpret the results obtained in terms of the physics in three-dimensional real space.

### LITERATURE

To facilitate access to the current literature a (fairly arbitrary) choice of papers is given, where further references can be found. Refs. 1-11 concern specific materials, 12-14 symmetry and 15-21 theoretical considerations.

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# Surface Science

The Belgian city of Ghent was host to the fifth European Conference on Surface Science: ECOSS from 24-27 August. This year's meeting, the local organisation of which was co-ordinated by the Rijksuniversiteit Ghent, followed its predecessors in maintaining a single oral session during the day with evenings devoted to poster presentations. Held in the Ghent International Congress Centre, a convivial atmosphere was assured by the close proximity of the auditorium, poster exhibition and coffee bar. The conference was accompanied by an industrial exhibition that covered a broad range of equipment from a complete ESCA photoelectron spectrometer to individual vacuum components, specimen manipulators, UHV pumps and residual gas analysers.

The ECOSS meetings have become established as the primary European forum in the field and as such attract a wide range of participants from outside as well as inside Europe. At these meetings the majority of papers are concerned with experimental studies of the phenomena occurring at single crystal surfaces. Nevertheless, there was also a wide range of other contributions: applied topics like the spectroscopy of helium microbubbles in metals and also fundamental theoretical work such as calculations of the electronic component involved in damping relative motion during the interaction of atoms and molecules at free electron surfaces.

The programme reflected the increased involvement of workers in problems of co-adsorption, surface reactions and prototype catalytic systems. Semiconductor surfaces and metal-semiconductor heterostructures were considered in detail as was the problem of surface segregation in binary alloys. Groups using established spectroscopic techniques like low energy electron diffraction have been producing convincing evidence for multiple layer relaxation at clean metal surfaces and have made structural determinations of some complicated adsorbate layers. Many papers were concerned with the electronic properties of various overlayer structures in which the principal tool is ultra-violet photoelectron spectroscopy. The importance of polarization measurements and considerations of adsorbate symmetry were clearly emphasised. At high photon energies, the availability of synchrotron radiation has led to a vigorous programme of study into surface core-level shifts and their interpretation. One morning was devoted to the new and rapidly expanding field of molecular-beam scattering from surfaces with talks on both high resolution inelastic scattering and accounts of studies into the nature of the interaction potential between helium atoms and surfaces.

Perhaps the most interesting and unusual presentation of the conference was the description of the new type of surface microscopy in which a current of electrons tunnelling between the sample under investigation and a sharp tip held in close proximity to it gives a direct microscopic image of the surface.

Not surprisingly, in a field where so many experimental techniques can be brought to bear on a particular problem, there are a number of simple systems where a conflict of evidence arises; oxygen adsorption on nickel is only one example of many. Paradoxically, as the various techniques are refined, the number of disparities appears to be on the increase but this is merely to say that our present understanding leaves much to be desired and a great deal remains to be revealed at future meetings in this series.

*W. Allison*