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EXPERIMENTAL INVESTIGATION OF 4-DIMENSIONAL SUPERSPACE
CRYSTALS

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Abstract The symmetry of incommensurate crystals can be described by higher dimensional space groups in the so called superspace approach. The basic ideas are explained and used for showing that superspace groups provide an adequate frame for analyzing experimental results on incommensurate crystals.

Consider a periodically distorted crystal for which the atomic positions are given by:

$$\vec{r}(\vec{n}, j) = \vec{r}_j + \vec{n} + \vec{A}f[\vec{q} \cdot (\vec{r}_j + \vec{n}) + \psi_j] \text{ any } \vec{n} \in \Lambda \quad (1)$$

where $\vec{n} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$ with n_i integers and $\vec{a}, \vec{b}, \vec{c}$ a basis of the lattice Λ ; \vec{r}_j is the position vector of atom j in the undistorted unit cell, $f(\psi) = f(\psi + 2\pi)$ is the modulation function, \vec{A} its amplitude and $\vec{q} = \alpha\vec{a}^* + \beta\vec{b}^* + \gamma\vec{c}^*$ the modulation wavevector. If at least one of the components α, β, γ of \vec{q} is irrational, Eq. (1) defines an incommensurate crystal, which does not have 3-dimensional lattice symmetry. However, the set of atomic positions is invariant with respect to the following discrete transformations:

$$\begin{aligned} \text{i)} \quad & \psi_j \rightarrow \psi_j + 2\pi z \text{ any integer } z \\ \text{ii)} \quad & \vec{n} \rightarrow \vec{n} + \vec{m} \text{ and } \psi_j \rightarrow \psi_j - \vec{q} \cdot \vec{m} \text{ any } \vec{m} \in \Lambda. \end{aligned} \quad (2)$$

One can say that a 4-dimensional symmetry is hidden in (1). This is also apparent if one looks to the diffraction pattern of (1) which gives the Fourier wavevectors \vec{k} of the corresponding crystal density and which can be described by 4 integers:

$$\vec{k} = (h, k, \ell, m) = h\vec{a}^* + k\vec{b}^* + \ell\vec{c}^* + m\vec{q}. \quad (3)$$

For $m = 0$ one has the normal Bragg reflections (main spots) corresponding to the average structure ($\vec{A} = 0$); the additional reflections are the satellites with $m \neq 0$ (see Fig. 1a).

To make the 4-dimensional lattice periodicity explicit one

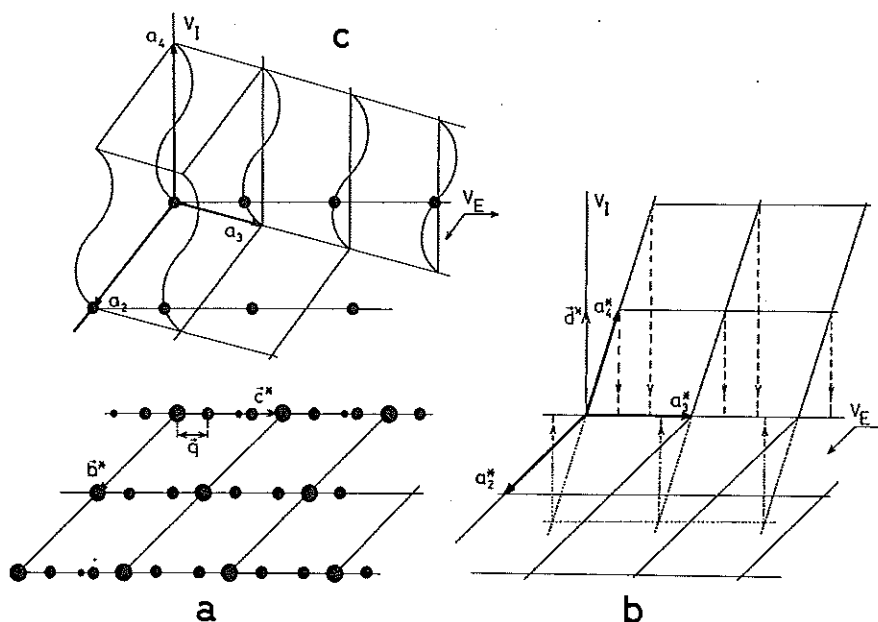


FIGURE 1 a) X-ray diffraction pattern of incommensurate crystal with $\vec{q} = \gamma\vec{c}^*$. Big dots indicate main spots, smaller dots indicate satellite reflections. b) Construction of superspace reciprocal lattice corresponding to diffraction pattern of 1a. c) Superspace crystal; dots indicate the real atom positions, obtained by intersecting the wavy pattern of the s.s. crystal with V_E (here and in 1b V_E is drawn as a 2-dimensional plane).

defines a 4-dim. superspace spanned by the 3-dim. external space V_E and an additional 1-dim. internal space V_I describing shifts of the modulation wave.¹ The wavevectors \vec{k} are now considered as a projection on V_E of a 4-dimensional reciprocal lattice Σ^* spanned by the basis vectors:

$$\begin{aligned} a_1^* &= (\vec{a}^*, 0) & a_3^* &= (\vec{c}^*, 0) \\ a_2^* &= (\vec{b}^*, 0) & a_4^* &= (\vec{q}, \vec{d}^*) \end{aligned} \quad (4)$$

where \vec{d}^* is a unit vector of the internal reciprocal space (see Fig. 1b). The 3-dimensional Fourier components $\hat{\rho}(h, k, \ell, m)$ are now interpreted as 4-dimensional Fourier components labelled by $\vec{k}_s \in \Sigma^*$. One then gets a so-called supercrystal with density $\rho_s(\vec{r}_s)$ given by:

$$\rho_s(\vec{r}_s) = \sum_{h, k, \ell, m} \hat{\rho}(h, k, \ell, m) e^{i\vec{k}_s \cdot \vec{r}_s} \quad (5)$$

which has a lattice Σ , with a basis reciprocal to that of Σ^* . The original point atoms become continuous lines in the s.s. crystal (see Fig. 1c).

The symmetry of (5) is described by a superspace group¹ and the superspace groups of a number of incommensurate crystals like K_2SeO_4 , TTF-TCNQ, TTF-I, 2H-TaSe₂ and $Hg_{3-\delta}AsF_6$ have been identified.

MORPHOLOGY

The growth form of single crystals reveals on a macroscopic scale the underlying microscopic structure. If the latter has a 4-dimensional symmetry one expects that this should appear in the morphology as well. Indeed in Rb_2ZnBr_4 (and Rb_2ZnCl_4) in the incommensurate phase, apart from the main faces, corresponding to the average structure, one observes additional so called satellite faces, characterized by 4 Miller indices $(hk\ell m)$.^{2,3} This labeling is justified by the fact that these faces are perpendicular to the corresponding k vectors of Eq. (3). The main faces thus appear as a special case, the $m = 0$ one (see Fig. 2).

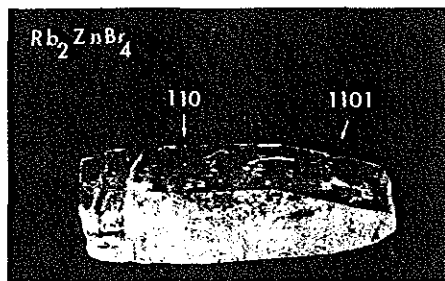


FIGURE 2 Single crystal of Rb_2ZnBr_4 showing large satellite face indexed as 1101.

LATTICE VIBRATIONS

In the superspace description the Hamiltonian of the system will depend on the internal coordinate τ as well because of the potential energy term which necessarily reflects the crystal structure. Furthermore this Hamilton operator can be made invariant with respect to the superspace group of the crystal and one can then apply group theory for characterizing the normal vibrational modes and their selection rules.^{4,5}

4-dimensional lattice translation symmetry leads according to the Bloch theorem, to the following ansatz for the normal modes:

$$\vec{u}(\vec{n}, \tau) = \sum_{\vec{k}} \vec{u}_{\vec{k}} e^{i(\nu\tau + \vec{k} \cdot \vec{n} - \omega t)}. \quad (6)$$

Using (6) and a simple model of modulated spring constants, one can calculate the new eigenfrequencies which are in fair agreement with experiment.⁵

A 4-dimensional crystal should also have $\omega = 0$ modes: 3 con-

nected with rigid translations of the crystal in 3 independent space directions and the 4th one being related to a rigid translation in the internal space, corresponding to a phase shift of the modulation. This so called phason mode has indeed been observed in ThBr_4 and Biphenyl.⁶

NUCLEAR MAGNETIC RESONANCE

The N.M.R. spectrum of a crystal depends on the Electric Field Gradient (EFG) tensor which has to be invariant with respect to its space group, and reflects the pointsymmetry of the atom measured. In the I-phase such pointsymmetry is very low and one expects to find EFG tensors of general form. This is not what has been observed in N.M.R. spectra of Rb_2ZnBr_4 and Rb_2ZnCl_4 ⁷ and one can show that it is a consequence of the superspace group symmetry of those crystals.⁸

In conclusion, the analysis as discussed above, though far from being complete, clearly indicates the relevance of the superspace approach to understanding the physical properties of incommensurate crystals.

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