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ELECTRONIC BANDSTRUCTURE OF AN INCOMMENSURATE CRYSTAL

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The consequences of an incommensurate lattice modulation on the electronic energy levels have been studied by optical transmission experiments on Rb_2ZnBr_4. The results are analyzed with a simple tight-binding model in which the superspace symmetry of the crystal is taken into account.

The lattice translational symmetry of crystalline matter leads to the well known concepts of the Brillouin zones, Bloch electrons, phonons and the like. In a crystal where the lattice is periodically distorted with a period that is incommensurate with the underlying lattice, this translational symmetry is broken. Nonetheless, incommensurate crystals are perfectly ordered and can be described by higher dimensional so-called superspace groups.[1] In this paper we will show how this superspace approach provides a natural framework to understand their electronic bandstructure as well.

Consider a crystal which is modulated along one crystallographic axis only, and therefore can be described by a one-dimensional model. In the tight-binding approximation, the Schrödinger equation for a sinusoidally modulated linear chain with states $|\psi_n\rangle$ localized on the nth atom can be written as:

$$W_{n+1}C_{n+1} + W_nC_{n-1} + (E_n - E)C_n = 0 \qquad (1a)$$

where C_n are the coefficients of the eigenfunctions $|\psi\rangle = \sum_n C_n|\psi_n\rangle$, E_n are the atomic energy levels, W_n represent the nearest neighbor interaction terms, which as a consequence of the lattice modulation will become modulated as well,

$$W_n = W_o(1 + \beta \cos(qna + \phi)) \qquad (1b)$$

a is the lattice constant of the undistorted chain, q the modulation wavevector and ϕ a phase factor. The parameter β will depend on the modulation amplitude and is zero in the normal (N-) phase. For an incommensurate modu-

lation $2\pi/q$ is irrational with respect to a and Eq. (1) does not have lattice symmetry. However, W_n is invariant under the following set of discrete transformations:

$$\begin{array}{lll} 1)\ n \to n + m & \phi \to \phi - qma & \text{integer } m \\ 2)\ n \to n & \phi \to \phi + 2\pi z & \text{integer } z. \end{array} \qquad (2)$$

These translations form a (1 + 1)-dimensional lattice in the superspace that can be formed by the normal space and an additional defined internal space.[1,2] This means that Eq. (1) does have a hidden 2-dimensional lattice symmetry, with all the coefficients depending on n and the phase ϕ: $W_n = W(n,\phi)$, etc. This also implies that the wavevectors k still form a valid representation for the electron wave functions.[2,3] Therefore, we can again apply the Bloch theorem and hence the solutions are of the form

$$C(n,\phi) = e^{ikna} \sum_{\nu} u^{\nu} e^{i\nu(qna+\phi)} . \qquad (3)$$

The Fourier expansion of Eq. (3) is a result of the periodicity in $(qna + \phi)$. By using Eq. (1) and (3) we can now calculate the new energy levels in the incommensurate (I-) phase. As a result of the modulation, each original level $E_n(k)$ splits up in a series of levels labelled by the index ν: $E_n^{\nu}(k)$. Since to a good approximation the modulation is sinusoidal[4] the main levels will be $\nu = 0$ and $\nu = \pm 1$. The effects of the modulation are illustrated in the schematic band picture of Fig. 1.

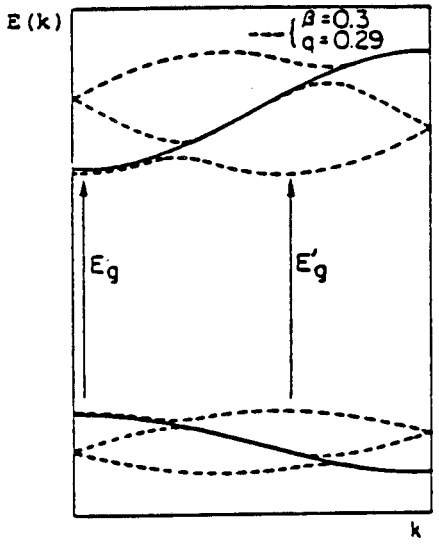

Fig. 1. Electronic bandstructure of an incommensurable modulated crystal (see text for parameters).
——— normal phase
- - - - - incommensurate phase

These results hold for the valence (E_v) as well as the conduction band (E_c). We therefore expect absorption edges to appear at

$$E \geq E_c^{\nu}(k) - E_v^{\nu'}(k') \quad \text{for } \nu,\nu' = 0,\pm 1. \qquad (4)$$

The vales for k and k' are given by the extrema of the conduction and valence band and depend on the real band structure of the crystal. However, without knowing the latter in detail, this simple model can give a qualitative understanding of the experimental results.

The incommensurate phase of Rb_2ZnBr_4 appears below T_i = 355 K and is characterized by an orthorhombic basic structure with space group Pcmn

and a displacive modulation with wavevector $\vec{q} = \vec{\gamma c}^* = 0.3\vec{c}^*$.[4] Single crystals were grown from an aqueous solution and transmission spectra in the bandgap region were recorded with a spectrometer.

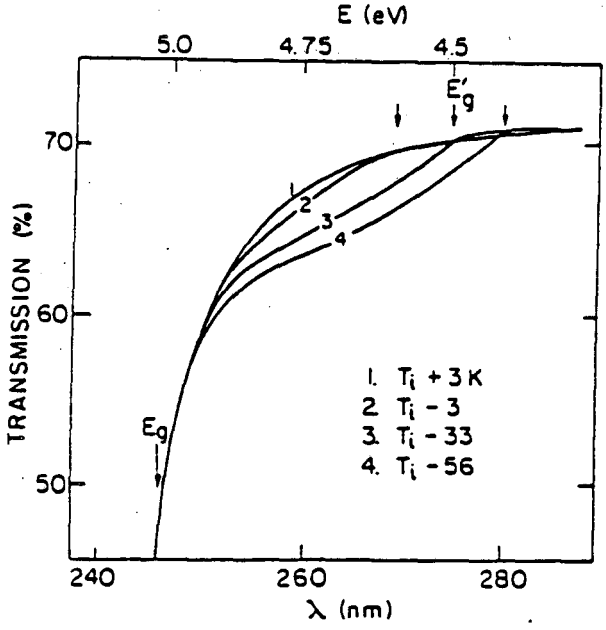

Fig. 2. Transmission spectra of Rb_2ZnBr_4 in the region of the bandgap E_g (defined by extrapolating to zero transmission), showing the appearance of a new absorption edge (E'_g) in the I-phase ($T < T_i$). The horizontal axis refers to spectrum 1; spectra 2, 3, and 4 are shifted to have their E_g overlap.

Figure 2 shows the results for temperatures above and below T_i; the spectra have been shifted with respect to each other to correct for the temperature dependence of the main gap at E_g.

In the N-phase, the only meaningful levels are the $\nu = \nu' = 0$ leading to the main absorption gap $E_g = E_c^o(k) = E_v^o(k')$ which causes the drop in transmission around 5 eV in Fig. 2. In the I-phase, additional absorption can occour involving $\nu, \nu' = \pm 1$, causing the onset of additional absorption at E'_g. The transition probability for these levels will be a measure of the modulation strength. Therefore, if we write for the absorption coefficient $\alpha^i = \alpha^n + \Delta\alpha$, where i and n refer to the I- and N-phases, respectively, $\Delta\alpha$ should be proportional to β. The experimental results for $\Delta\alpha$ can be fitted with $\Delta\alpha = a\sqrt{T_i - T}$ with $a = 0.087\ cm^{-1}K^{-1/2}$ and $T_i = 357 \pm 1$ K.

From our numerical results for $E_n^\nu(k)$ it follows that this new absorption edge involves $k = q$ and $k = K - q$, and that $E_g - E'_g$ is almost constant for $\beta < 0.3$ and is proportional to β^2 for $\beta > 0.3$. Therefore, we expect $E_g - E'_g \sim (T_i - T)$ (for Rb_2ZnBr_4 the temperature dependence of q can be neglected in the region of interest). The temperature dependence of $E_g - E'_g$ is plotted in Fig. 3 and is in good agreement with these predictions.

In conclusion, we have shown how the superspace approach, introduced to describe the microscopic symmetries of incommensurate crystals, provides a natural framework to understand their electronic bandstructure as well. The recovery of lattice translational symmetry leads again to a Bloch formalism

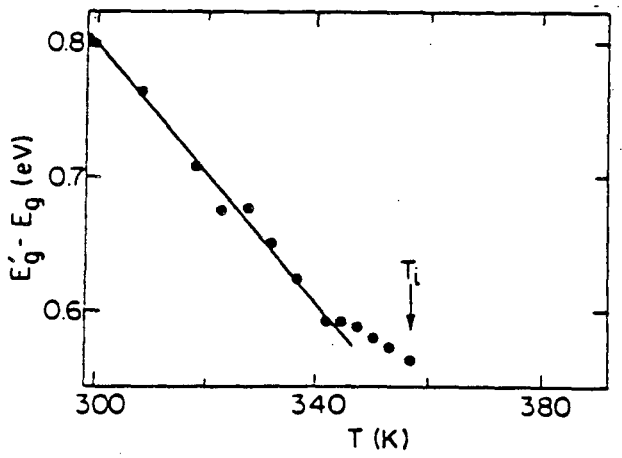

Fig. 3. Temperature dependence of new absorption edge E'_g relative to that of E_g.

(though now in a higher dimensional space) which can be used to solve a simple tightbinding model. The resulting predictions of new energy levels and their dependence on the modulation parameters are confirmed by optical absorption spectra in the bandgap region of the modulated crystal Rb_2ZnBr_4. The same approach can also be applied to charge density wave systems, where now the E_n instead of the W_n will be modulated (see Ref. 5).

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