New Electronic Levels in the Incommensurate Crystal Rb_2ZnBr_4

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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 show the appearance of new energy levels and are analyzed with a simple tight-binding model in which the superspace symmetry of the crystal is taken into account.

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The absence of lattice translational symmetry in incommensurate systems breaks down such fundamental concepts as Brillouin zones and Bloch electrons. This can also lead to interesting new properties as have been observed in so-called charge-density-wave systems.[1]

In this paper I consider the electronic band structure of a crystal with a modulated lattice and present experimental evidence for the appearance of new energy levels. I show how the superspace approach, introduced to describe the microscopic symmetries of incommensurate crystals,[2] provides a natural framework for understanding optical transitions as well.

The incommensurate (I) phase of Rb_2ZnBr_4 appears below $T_i \cong 355$ K and is characterized by an orthorhombic basic structure with space group *Pcmn* and a displacive modulation with wave vector $q = \gamma c^* = 0.3c^*$.[3] Single crystals were grown from an aqueous solution and transmission spectra in the band-gap region were recorded with a spectrometer.

Figure 1 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 E_g. In the I phase ($T < T_i$) a new absorption edge appears below the main gap at E_g' which shifts in energy and becomes stronger with decreasing temperature.

Since the crystal is modulated along one crystallographic axis only, we will use a one-dimensional model to understand the basic features induced by this modulation.

In the tight-binding approximation, the Schrödinger equation for a linear chain with states $|\psi_n\rangle$ localized on the nth atom can be written as

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

where C_n are the coefficients of the eigenfunctions $|\psi> = \sum_n C_n|\psi_n>$, E_n are the atomic energy levels, and W_n represent the nearest-neighbor interaction terms. As a consequence of the lattice modulation the W_n (which depend on the overlap intergals between neighboring atoms) will become modulated as well. For the case of a simple sinusoidal modulation we will have

$$W_n = W_0[1 + \beta\cos(qna + \phi)]. \quad (2)$$

Here a is the lattice constant of the undistorted chain, q the modulation wave vector, 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 modulation $2\pi/q$ 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:

$$\begin{aligned} &n \rightarrow n + m, \quad \phi \rightarrow \phi - qma, \quad \text{integer } m; \\ &n \rightarrow n, \quad \phi \rightarrow \phi + 2\pi z, \quad \text{integer } z. \end{aligned} \quad (3)$$

These translations form a (1+1)-dimensional lat-

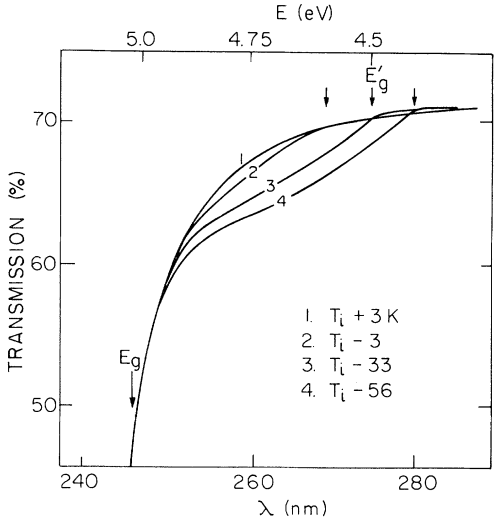

FIG. 1. Transmission spectra of Rb_2ZnBr_4 in the region of the band gap E_g (defined by extrapolating to zero transmission), showing the appearance of a new absorption edge (E_g') in the I phase ($T < T_i$). The horizontal axis refers to spectrum 1; spectra 2–4 are shifted to have their E_g overlap.

tice in the superspace that can be formed by the normal space and an additional defined internal space.[2,4] This means that Eq. (1) does have a hidden two-dimensional lattice symmetry, with all the coefficients depending on n and the internal parameter $\tau(=\phi)$: $W_n = W(n,\tau)$, etc. This also implies that the wave vectors k still form a valid representation for the electron wave functions.[4,5] Therefore, we can again apply the Bloch theorem and hence the solutions are of the form

$$C(n,\tau) = e^{ikna} u(qna+\tau), \tag{4a}$$

$$= e^{ikna} \sum_\nu u^\nu e^{i\nu(qna+\tau)}. \tag{4b}$$

The Fourier expansion of Eq. (4b) is a result of the periodicity in τ. Inserting Eqs. (4) and (2) in Eq. (1) and taking terms with the same factor $e^{i\nu\tau}$ leads to an infinite set of coupled equations of the form

$$A_\nu u^{\nu-1} + D_\nu u^\nu + B_\nu u^{\nu+1} = 0, \quad \text{integer } \nu, \tag{5}$$

where A, D, and B are functions of k, E_n, W_n, and the modulation parameters. From Eq. (5) the new energy levels in the I phase can be calculated. In first-order approximation, with neglect of the coupling between different Fourier coefficients $\nu' \neq \nu$, this gives

$$E_n^\nu(k) = E_n + 2W_0 \cos(k+\nu q), \quad \text{integer } \nu. \tag{6}$$

Equation (6) indicates that in the I phase each original level labeled by n splits up into a series of levels labeled by the index ν, but it neglects their interactions. For a more realistic calculation one has to take the coupling between ν and $\nu' \neq \nu$ into account, and since to a good approximation the modulation is sinusoidal[3] the main levels will be $\nu = 0$ and $\nu = \pm 1$. Though this can be solved exactly, the complete results cannot be given in a simple analytical expression in k and will be treated elsewhere.[6] However, for some k values one can get approximate solutions; e.g., at $k = 0$

$$E_n^0(0) \simeq E_n + 2W_0 + \frac{\beta^2 W_0}{2}\left(\frac{1+\cos q}{1-\cos q}\right),$$

$$E_n^1(0) \simeq E_n + 2W_0\cos q - \frac{\beta^2 W_0}{2}\left(\frac{1+\cos q}{1-\cos q}\right), \tag{7}$$

$$E_n^{-1}(0) \simeq E_n + 2W_0\cos q,$$

whereas for $k = q/2$ terms linear in β are present. For the $\nu = \pm 1$ levels extrema appear at $k = q$ and $k = K - q$ (where K is the Brillouin zone wave vector) having a β^2 dependence for $\beta \gg 0$.

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

$$E \geq E_c^\nu(k) - E_v^{\nu'}(k') \quad \text{for} \quad \nu, \nu' = 0, \pm 1. \tag{8}$$

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

In the N phase, the only meaningful levels are the $\nu = \nu' = 0$, leading to the main absorption gap $E_g = E_c^0(k) - E_v^0(k')$ which causes the drop in transmission around 5 eV in Fig. 1. In the I phase, additional absorption can occur involving $\nu, \nu' = \pm 1$, causing the onset of additional absorption at E_g' [see Fig. 1; experimentally, E_g' has been determined as the energy for which the transmission drops below that of the normal spectrum (at $T = T_i + 3$ K), with a maximum error of 0.02 eV]. 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 $\Delta\alpha$ are plotted in Fig. 2 and can be fitted by $\Delta\alpha = a(T_i - T)^{1/2}$ 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(a) and is in good agreement with these predictions.

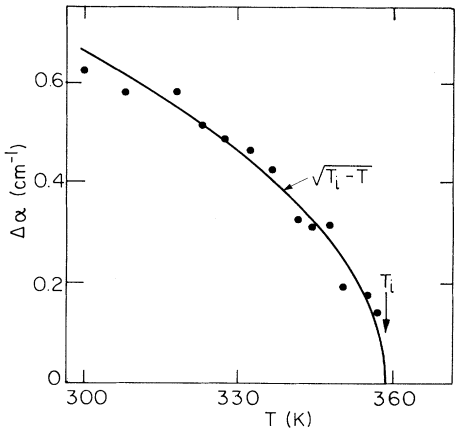

FIG. 2. Temperature dependence of absorption increase $\Delta\alpha$ (for a fixed value of $E_g - E_g'$) in the I phase.

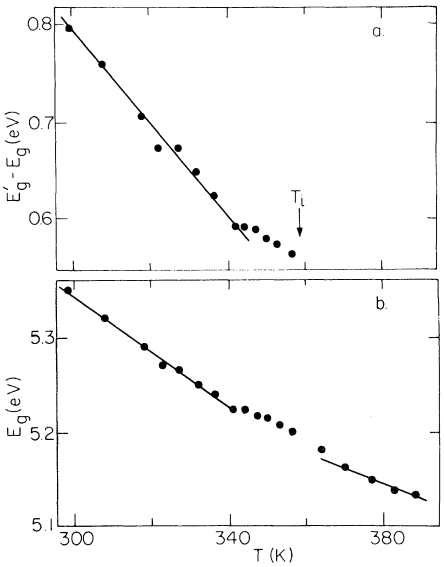

FIG. 3. (a) Temperature dependence of new absorption edge E_g' relative to that of E_g. (b) Temperature dependence of main gap E_g in the N and I phases. The solid lines show the linear fits.

In the I phase the $\nu = 0$ levels are still good solutions but will be perturbed via the parameter β. This means for the main gap that

$$E_g^i = E_g^n + \beta F + \beta^2 G, \tag{9}$$

where the constants F and G will depend on the actual band structure. The experimental results are plotted in Fig. 3(b) and show qualitative agreement. For $T \ll T_i$ the original linear T dependence of E_g^n has been increased by a linear term, indicating $F \ll G$. However, close to T_i the data cannot be fitted with two constants F and G only, presumably because of additional effects due to soft lattice modes.

In conclusion, I have observed the appearance of new absorption levels in an incommensurate crystal. I have shown how the superspace approach leads to a generalization of the Bloch theorem and can be used to solve a simple tight-binding model for electrons in an incommensurate potential. The temperature dependence of the extra absorption indicates that the density of states involved in these transitions increases roughly linearly with the modulation potential whereas the energy levels themselves shift with the square of this as a result of the effect of the modulation on the interaction between localized atomic levels.

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