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Influence of stacking disorder on the electronic properties of layered semiconductors

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The influence of stacking disorder on the electronic properties of layered materials is discussed. It is shown that the problem of stacking disorder is equivalent to the problem of one-dimensional disordered chains. Consequently, the presence of stacking disorder leads to a localization of the electronic wave functions in the direction perpendicular to the layers. The localization lengths are estimated in the framework of a tight-binding model. Results of dc measurements on GaSe indicate that transport along the c axis is indeed strongly affected by stacking disorder.

For a long time, layered materials have been considered as essentially two-dimensional solids, i.e., their electronic properties have been described in terms of two-dimensional band structures, where the layer-layer interaction is neglected. Support for this drastic simplification came from the extreme weakness of the *mechanical* coupling of the layers. In the course of the last few years, however, there has been increasing evidence that layered materials behave in many respects like three-dimensional crystals. For example, the electronic transport properties of GaSe at high temperatures show that this layered semiconductor cannot be understood in terms of a two-dimensional model. The same conclusion can be drawn from optical data[1] and from band-structure calculations.[2]

In view of this, the interlayer interaction cannot be neglected in a discussion of the electronic properties of such crystals. However, the layers can be stacked in a variety of ways. The corresponding stacking energies are nearly the same, the differences arising only from third and more distant neighbor interactions. Consequently, it is necessary to investigate how different stackings affect the electronic properties. In this context, the band structures of different polytypes of PbI_2 have been investigated recently.[3] These calculations readily explain the differences observed in the optical properties of the $2H$ and $4H$ polytypes PbI_2. In the present paper, an attempt is made to go one step further and to discuss the influence of stacking *disorder*, i.e., the effect of a nonperiodic stacking sequence. Indeed, since the stacking-fault energy in layered materials is small, *real* crystals grown at high temperatures usually exhibit a nonperiodic stacking sequence.

As an example, we consider the case of GaSe. Three different stacking types are found in this material.[1] They are denoted as β, γ, and ϵ. For the ϵ and γ stackings, the successive layers can be generated from one primitive layer by pure translations, whereas an additional rotation through 60° about the c axis is required in the β stacking. It is noteworthy that these operations do not destroy the translational symmetry of the hexagonal two-dimensional Bravais lattice of a single layer. Thus, if the real crystal contains only the β, γ, and ϵ stackings distributed at random, the full crystal still obeys the translational symmetry of the single layer. Along the layer normal, however, translational symmetry is destroyed. These structural properties will become important when a model is developed which describes the influence of stacking disorder on the electronic properties.

Stacking disorder can only influence those properties which depend on the layer-layer interaction in the perfect crystal also. In Fig. 1, the band structure of β-GaSe is shown as calculated by Schlüter by the pseudopotential method.[2] The influence of the layer-layer interaction on the electronic states can be estimated from the dispersion of the different bands in the direction $\vec{k} \parallel \vec{c}$, i.e., along the $\Gamma - A$ axis. We find that the lower valence bands show only a very small dispersion along this axis. Therefore, they can be considered two dimensional; that is, they are independent of the layer-layer interaction and consequently the existing stacking order will not influence the corresponding electronic states. However, other bands like the uppermost valence band and the lowest conduction band show a dispersion along Γ-A which is comparable to that in the other directions. These bands are three-dimensional and their shape depends strongly on the interlayer interaction. It may be expected, therefore, that they also depend on the actual stacking disorder in a real GaSe crystal.

In order to investigate this dependence, electronic transport measurements have been performed on GaSe. The dc conductivity parallel with the layers and the Hall effect in a magnetic-field parallel with c have been measured by the Van der Pauw technique.[4] The dc conductivity across the layers has been measured by the Valdes technique,[5] in which four-point contacts are aligned on a cleaved face of a thick sample. Conductivity along the layers is

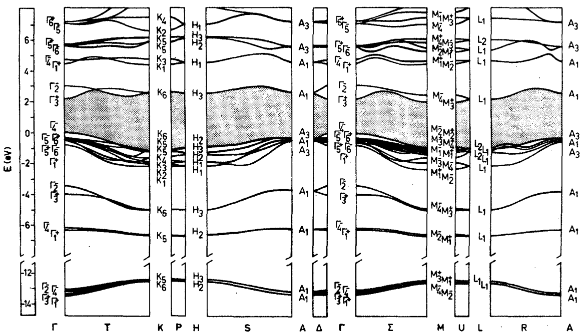

FIG. 1. Band structure of β-GaSe.

governed by a hole mobility which can be written

$$\mu \sim T^{-\gamma}, \tag{1}$$

where $\gamma = 1.9 \pm 0.1$. This behavior can be explained as band conductivity of holes scattered by optical phonons which modulate the layer thickness.[6] Direct measurements of the drift mobility by the time-of-flight technique show that the mobility parallel to c exhibits the same behavior[7]

$$\mu \sim T^{-\gamma}. \tag{2}$$

Since short-range interaction with optical phonons is an isotropic process, the anisotropy observed in these measurements is given by the mass ratio $m_\perp/m_\parallel$ which is found to be of the order of 4. In the limit of high temperatures, the anisotropy $\sigma_\parallel/\sigma_\perp$ reaches the same value. At low temperatures, however, the anisotropy of the conductivities obeys the relation

$$\frac{\sigma_\parallel}{\sigma_\perp} = A\, e^{-\Delta E/kT}, \tag{3}$$

where the preexponential factor A is again of the order of $m_\perp/m_\parallel$. Because of this high value of A, a description of $\sigma_\parallel$ in terms of hopping between the *tails* of strongly localized states can be excluded.

This behavior is always found at the lowest temperature in our measurements (77 °K). Equation (3) suggests that conductivity parallel with the c axis differs from that in the layers by a process involving an activation energy ΔE. This activation energy turns out to be strongly sample dependent. It is in the range of 15–100 meV. Clearly, the observed anisotropy (3) cannot be explained in terms of the band structure. In the following, we will show that this activation energy can be interpreted as an effect of stacking disorder on the electronic states close to the band edge. To this end, we consider the single-band Hamiltonian

$$H = \sum_{n\vec{k}} \epsilon_n(\vec{k}_\perp)\,|n\vec{k}_\perp\rangle\langle n\vec{k}| + \sum_{nn'}\sum_{\vec{k}_\perp\vec{k}_\perp'} V(n\vec{k}_\perp, n'\vec{k}_\perp')\,|n\vec{k}_\perp\rangle\langle n'\vec{k}_\perp'|, \tag{4}$$

where $\epsilon_n(\vec{k}_\perp)$ is the band structure of an isolated layer n and where $|n\vec{k}_\perp\rangle$ are the corresponding eigenstates. The first term of (4) describes the Hamiltonian for several noninteracting layers, whereas the second term accounts for the interaction between layers n and n'. This interaction is specified by the matrix elements $V(n\vec{k}_\perp, n'\vec{k}_\parallel')$. If we now assume that only stackings of the type β, ϵ, and γ are present in real crystals of GaSe, translational invariance perpendicular to the c axis is preserved. The eigenfunctions, therefore, are still Bloch functions for $\vec{k}_\perp$, and consequently the overlap matrix V is diagonal in $\vec{k}_\perp$ and $\vec{k}_\perp'$. Under these circumstances the Hamiltonian reduces to a sum of one-dimensional Hamiltonians

$$\begin{aligned} H &= \sum_{\vec{k}_\perp}\Big(\sum_n \epsilon_n(\vec{k}_\perp)\,|n\vec{k}_\perp\rangle\langle n\vec{k}_\perp| \\ &\qquad + \sum_{nn'} V(n, n', \vec{k}_\perp)\,|n\vec{k}_\perp\rangle\langle n'\vec{k}_\perp|\Big) \\ &= \sum_{\vec{k}_\perp} H_{1\text{-dim}}(\vec{k}_\perp). \end{aligned} \tag{5}$$

The problem of stacking disorder is thus transformed into a problem of one-dimensional disordered chains, which can be solved readily.

Disorder may be introduced in Eq. (5) in two ways: either by statistical fluctuations of the ϵ_n ("diagonal disorder") or by statistical fluctuations of the overlap matrix elements V ("nondiagonal disorder"). Both types of disorder affect the electronic properties in essentially the same way. In the following we assume that stacking disorder acts on the electronic states primarily through the fluctuations of overlap matrix elements between the single layer functions only, i.e., we restrict ourselves to the discussion of nondiagonal disorder.

Let us consider the Hamiltonian

$$H_{1\text{-dim}} = \epsilon \sum_n |n\rangle\langle n| + \sum_{nn'} V(n, n')\,|n\rangle\langle n'| \tag{6}$$

describing a one-dimensional disordered chain. For the numerical treatment of this Hamiltonian, we have considered a finite chain of 1001 atoms, the interaction being restricted to nearest neighbors only. Disorder is described by statistical fluctuations of $V(n, n\pm 1)$ over two discrete values V_1 and V_2. The probabilities of V_1 and V_2 are given by x and $1-x$, respectively. Disorder is thus specified by the probability x and the relative deviation

$$\Delta = (V_1 - V_2)/V_2 \tag{7}$$

of the overlap matrix elements V_1 and V_2. It is well known that one-dimensional disorder leads to a localization of the eigenfunctions which therefore extend over a finite region only.[8] In our model this means that stacking disorder leads to eigenfunctions which are nonzero over a finite number of layers only. The physical properties obviously depend on the degree of localization and we define a localization length L as the region over which 80% of the eigenfunction Ψ is localized. In other words, if

$$\Psi = \sum_{n=1}^{N} a_n |n\rangle \qquad (8)$$

and

$$\sum_{n=i}^{l} |a_n|^2 = 0.8 \,, \qquad (9)$$

then

$$L = \min(l - i + 1) \,. \qquad (10)$$

Outside this region, Ψ decreases exponentially.[9] We have computed the localization length L and the density of states $n(E)$ for several values of the parameters x and Δ. In Fig. 2, we show the results for a relative deviation of V_1 and V_2 of 8% and a concentration of 50%. This choice of Δ appears to be reasonable for the case of GaSe, in view of the difference of 50-meV observed between the direct exciton line of the β and of the ϵ and γ polytypes.[10] The results are normalized to a bandwidth of 1 eV ($V_2 = 0.5$ eV). This corresponds to the bandwidth of the upper valence band of Fig. 1.

The results shown in Fig. 2 have been obtained by averaging over four statistical distributions of V_1 and V_2. The top of Fig. 2 shows the number of states as a function of energy in the immediate vicinity of the band edge. As expected, we find that the $1/\sqrt{E}$ singularity of the periodic chain is somewhat blurred by disorder. Below, the calculated localization length L is given as a function of energy. L is found to be a roughly linear function of energy and it goes to zero at the band edge. We can thus conclude that stacking disorder confines the electron states close to the band edge to a few layers only.

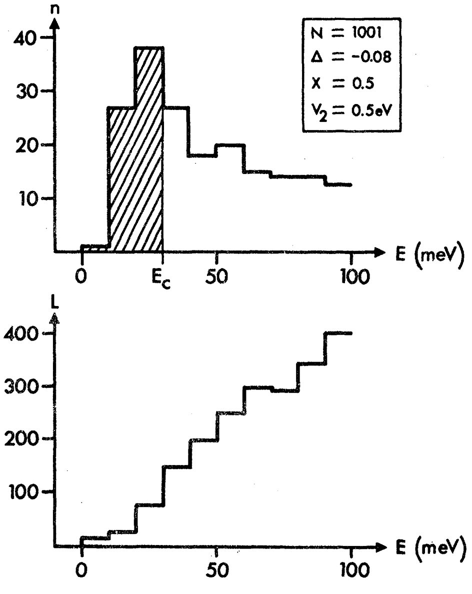

FIG. 2. Density of states (above) and localization length (below) of one-dimensional disordered chains near the band edge.

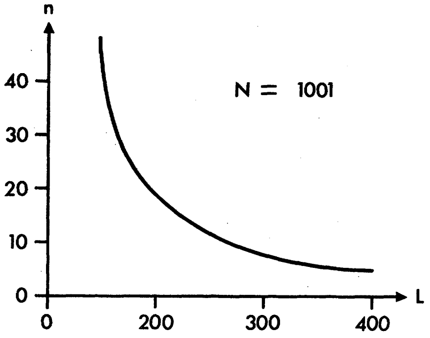

FIG. 3. Percolation limit for one-dimensional chains.

We are now in a position to estimate the influence of localization on the dc conductivity. The charge carriers have to travel from one side of the crystal to the other in order to contribute to the dc. In a first step, we consider random distributions of states of localization length L and we calculate the average number n_c of such states required to cover the chain from end to end. The result of this simple percolation calculation is shown in Fig. 3. We now argue as follows: The charge carriers can exchange with the lattice an energy which is typically of the order of kT. We therefore consider the carriers within an interval kT around the energy E. In this interval, the average localization length is $L(E)$. We then compare the number of states $n(E)$ with the critical number $n_c(L)$: A contribution to the dc transport across the layers is expected only if the chain is entirely covered by the states belonging to the energy interval, i.e., if $n > n_c$. In this manner, a lower estimate for a critical energy E_c is obtained such that the contribution to the dc of carriers with $E < E_c$ can be neglected. In our measurements on GaSe, kT was of the order of 10 meV. In this case, one finds that all charge carriers in the shaded area of Fig. 2 do not contribute to transport across the layers, although they participate in the transport along the layers. We can thus conclude that the critical energy E_c is a lower limit for the activation energy ΔE which appears in the expression (3) of the anisotropy.

The mechanism which we propose for conduction along c and for $E > E_c$ is formally a hopping process. However, in contrast with the usual picture where variable-range hopping occurs via the small overlap between the exponential tails of localized states, it occurs here via the large overlap between states which extend over many layers with a nearly constant amplitude. The high value of A in Eq. (3) can thus be understood. Below E_c, hopping occurs via the exponential tails. This contribution can be neglected at all but the lowest temperatures. The localized states below E_c should make a sizable contribution to the ac conductivity. In this manner one can explain the frequency-dependent conductivity

$$\sigma_{\parallel} \sim \omega^{\gamma}, \quad \gamma \simeq 0.8 \tag{11}$$

observed in several layer compounds such as SnS_2,[11] ZrS_2, and HfS_2.[12]

In conclusion, the following points should be stressed: Because of the high incidence of stacking disorder in layer structures, these materials are ideally suited for an investigation of the properties of one-dimensional disordered systems. Moreover, we have shown that the anisotropy of the dc conductivity in GaSe is not an effect of the band structure but rather one of disorder. The optical properties of layered semiconductors near the absorption edge should yield more information on the disorder-induced localization of the wave functions.

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