

## Influence of stacking disorder on the dc conductivity of layered semiconductors

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The stacking disorder present in many layer materials leads to a localization of the electronic states along the layer normal. It is shown that the anisotropy of the dc conductivity can be calculated in terms of a one-dimensional hopping model. Numerical results are given for the dependence of the anisotropy, both on the concentration of the stacking faults and on the perturbation produced by a single stacking fault. The experimental anisotropy of GaSe is discussed in terms of the presented model.

### I. INTRODUCTION

Many layer materials exhibit a large amount of stacking faults. As was shown in a recent paper<sup>1</sup> the anisotropy of the dc transport in those materials is mainly produced by this type of disorder and not by the intrinsic structural anisotropy of the perfect crystal. In the case of GaSe, for example, which usually is *p* type, the uppermost valence band is known to be formed mainly by the  $p_x$  orbitals on the Se atoms, with considerable overlap both across and within the layers.<sup>2</sup> The resulting effective masses, therefore, cannot explain the strong anisotropic behavior of the dc conductivity found experimentally. This anisotropy is well described by<sup>1</sup>

$$\sigma_{\parallel}/\sigma_{\perp} = Ae^{-\Delta E/kT}, \quad (1)$$

where  $\sigma_{\parallel}$  and  $\sigma_{\perp}$  are the conductivities parallel and perpendicular to the crystallographic *c* axis, respectively.

In GaSe the activation energy  $\Delta E$  is strongly sample dependent and of the order of 10 to 100 meV. As was shown<sup>1</sup> the disorder due to the stacking faults is sufficient to localize the electron states along the layer normal. If we consider only the most probable stackings of the  $\beta$ ,  $\gamma$ , and  $\epsilon$  type between adjacent layers, the total crystal remains still invariant under the primitive translations parallel to the layers. The electron states, therefore, transform like Bloch functions under these translations and dc transport parallel to the layers is not affected by the presence of stacking disorder. Perpendicular to the layers, however, the transport is hoppinglike due to the localization of the electronic states. The aim of the present paper is to replace the estimate of the hopping activation energy in Ref. 1 by a more detailed model calculation. In particular, we discuss the dependence of the resulting anisotropy on the parameters describing the disorder.

### II. DERIVATION OF THE HOPPING RATES

As shown in Ref. 1 the single-band Hamiltonian for the electrons can be written as a sum over one-dimensional Hamiltonians, i.e.,

$$H = \sum_{\vec{k}} \left( \epsilon_n(\vec{k}_{\perp}) |n \vec{k}_{\perp}\rangle \langle n \vec{k}_{\perp}| + \frac{1}{2} \sum_{nn'} V(n, n', \vec{k}_{\perp}) |n \vec{k}_{\perp}\rangle \langle n' \vec{k}_{\perp}| \right). \quad (2)$$

The index  $n$  labels the different layers,  $|n \vec{k}_{\perp}\rangle$  are the two-dimensional Bloch functions with wave vector  $\vec{k}_{\perp}$  of an isolated layer.  $V(n, n', \vec{k}_{\perp})$  describes the coupling between different layers. For simplicity we shall assume that  $V(n, n', \vec{k}_{\perp})$  does not depend on  $\vec{k}_{\perp}$  and couples only adjacent layers, i.e.,  $n' = n \pm 1$ .

Following Ref. 1 we assume  $\epsilon_n(\vec{k}_{\perp})$  to be independent of the layer index  $n$ . For  $V(n, n \pm 1)$  we consider two values  $V_1$  and  $V_0$ : in the ordered case  $V(n, n \pm 1)$  is equal to  $V_0$ , stacking faults are described by the coupling  $V_1$ . These stacking faults are supposed to occur with a probability  $x$  and to be distributed randomly. The eigenvalues for the resulting Hamiltonian

$$H = \sum_{\vec{k}} \left( \epsilon(\vec{k}_{\perp}) \sum_n |n \vec{k}_{\perp}\rangle \langle n \vec{k}_{\perp}| + \sum_n V(n, n+1) |n \vec{k}_{\perp}\rangle \langle n+1, \vec{k}_{\perp}| \right) \quad (3)$$

can then be expressed as

$$E(i, \vec{k}_{\perp}) = \epsilon(\vec{k}_{\perp}) + \delta_i, \quad (4)$$

where  $i$  labels the different states of the one-dimensional Hamiltonian

$$H_{1\text{-dim}} = \sum_n V(n, n+1) |n \vec{k}_{\perp}\rangle \langle n+1, \vec{k}_{\perp}| \quad (5)$$

which has eigenvalues  $\delta_i$  independent of  $\vec{k}_{\perp}$ .

The eigenfunctions of the total Hamiltonian (3)

$$|i\vec{k}_\perp\rangle = \sum_n C_n^i |n\vec{k}_\perp\rangle \quad (6)$$

are linear combinations of the Bloch-like eigenfunctions of the single layers. These eigenfunctions are localized over some layers via the coefficients  $C_n^i$ . It should be noted that the localization length is independent of  $\epsilon(\vec{k}_\perp)$ , but depends on  $\delta_i$  only.

In order to construct a hopping-like model we have to consider the probability for a phonon-assisted transition of a carrier in state  $|i\vec{k}_\perp\rangle$  to a state  $|j\vec{k}'_\perp\rangle$ . Following Ambegaokar *et al.*<sup>3</sup> this can be written

$$P_{i\vec{k}_\perp \rightarrow j\vec{k}'_\perp} = M_{ij}^{\vec{k}_\perp \vec{k}'_\perp} \exp\left(-\frac{\max[E(i, \vec{k}_\perp), E(j, \vec{k}'_\perp)]}{kT}\right), \quad (7)$$

where the matrix element  $M_{ij}^{\vec{k}_\perp \vec{k}'_\perp}$  is only weakly temperature dependent and is proportional to the spatial overlap between the functions  $|i\vec{k}_\perp\rangle$  and  $|j\vec{k}'_\perp\rangle$ . Integrating Eq. (7) with respect to  $\vec{k}_\perp$  and  $\vec{k}'_\perp$  we have studied two limiting cases:

$$(i) M_{ij}^{\vec{k}_\perp \vec{k}'_\perp} = M_{ij}^0,$$

i.e., the matrix element is independent of  $\vec{k}_\perp$  and  $\vec{k}'_\perp$ .

$$(ii) M_{ij}^{\vec{k}_\perp \vec{k}'_\perp} = M_{ij}^0 \delta_{\vec{k}_\perp \vec{k}'_\perp},$$

i.e., only direct transitions are allowed. In both cases we obtain

$$P_{i \rightarrow j} = \sum_{\vec{k}_\perp, \vec{k}'_\perp} P_{i\vec{k}_\perp \rightarrow j\vec{k}'_\perp} = M_{ij}^0 A(T) \exp\left(-\frac{\max(\delta_i, \delta_j)}{kT}\right), \quad (8)$$

where  $A(T)$  is a polynomial of second order in temperature. This temperature dependence may be neglected with respect to the temperature dependence of the activation term.

The integration over  $\vec{k}_\perp$  and  $\vec{k}'_\perp$  has thus reduced our three-dimensional conductivity problem to a one-dimensional hopping problem. An explicit solution requires the knowledge of the distribution of the disorder energies  $\delta_i$  and of the matrix elements  $M_{ij}^0$ .

### III. ONE-DIMENSIONAL HOPPING MODEL

The disorder energies  $\delta_i$  are given by the eigenvalues of the Hamiltonian Eq. (5). The matrix elements  $M_{ij}^0$  are set proportional to the mutual overlap squared of the corresponding eigenfunctions. Following Ref. 1 we studied a finite chain of 1001 sites, which in our model means a stack of 1001 layers. At the band edges the eigenfunctions turn out to be strongly localized. The square

of the eigenfunctions is approximately constant over a certain length, but decreases rapidly outside of this region. We, therefore, can define the extent of the wave function by the length in which most of the corresponding charge (80% in this calculation) is confined. We have calculated these eigenvalues and corresponding localization lengths for several values of the disorder parameter

$$\Delta = (V_1 - V_0)/V_0 \quad (9)$$

and of the disorder concentration  $x$ . The corresponding density of states and the average extent of the wave functions are shown in Fig. 1 for some examples with different disorder parameter  $\Delta$  and a fixed concentration ( $x=0.5$ ). In these and the following figures we have assumed a total bandwidth of 1 eV as is appropriate for the uppermost valence band in GaSe.<sup>2</sup> The singularity in the density of states at the band edge disappears due to the disorder. The states near the band edge become more and more localized with increasing disorder.

We are now in the position to set up a classical conductance network appropriate to calculate the resulting conductivity. The centers of the localized eigenfunctions are connected by conductances proportional to  $P_{i \rightarrow j}$  [Eq. (8)]. This leaves us with an intricate network of interconnected conductors. The conductivity of this network is calculated numerically with the aid of Kirchhoff's equations. Since for low temperatures only states close to the band edge contribute to the current we can reduce the computational effort drastically including the 100 states with lowest energies only.

In Fig. 2 we show the temperature dependence of the calculated resulting conductivity for a typ-

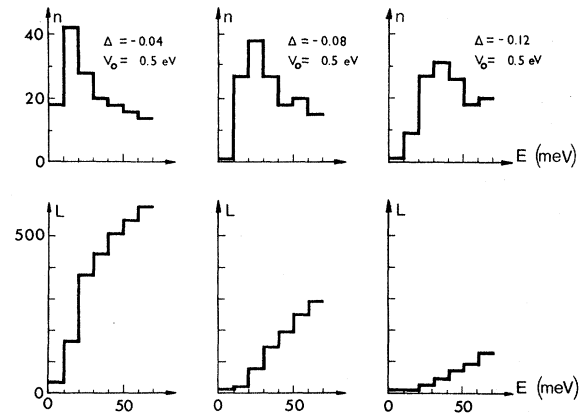


FIG. 1. One-dimensional densities of states  $n$  and localization lengths  $L$  (given in number of layers) for different  $\Delta$ .

ical example. The Fermi energy is placed at the band edge. The data points in this figure are averaged over 20 different calculations. The activation energy apparent from Fig. 2 may be explained by a simple percolation model (Fig. 3): We construct a sequence of states with lowest energies such that these states cover the entire chain. The maximum energy,  $E_{\text{perc}}$ , occurring in this sequence will be the maximum activation energy of the corresponding conductance and hence, at low temperatures, determine the sample conductivity. The results of this calculation are also plotted in Fig. 2. The activation energy  $E_{\text{perc}}$  is very close to that derived from the network calculation.

It should be borne in mind that this construction is valid for finite chains only. There is an extremely small but finite probability that the chain has an interruption at a given site. This finite probability causes with certainty an interruption for chains with an infinite number of sites. However, in order to describe the experiment, we have to deal with systems containing  $10^4$  to  $10^6$  sites only. These are relatively small numbers, so that interruptions can be neglected. This is also ascertained by numerical calculations where the number of sites was changed over a wide range ( $10^3$  to  $2 \times 10^5$ ). In these calculations the impedance per unit length was virtually independent of the number of sites.

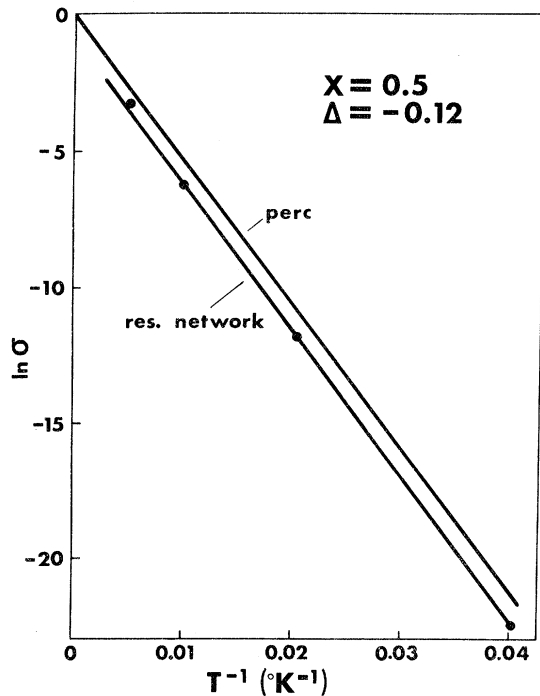


FIG. 2. Calculated conductivity as a function of temperature.

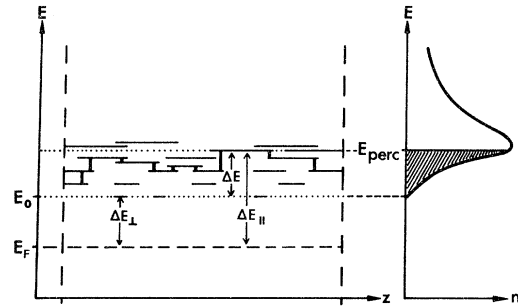


FIG. 3. Percolation model for the transport across the layers. The distribution and extension of the electronic states are represented by the horizontal lines.

In order to compare our results with the experimental situation, we shall now discuss the resulting anisotropy of the dc conductivity: Since the states behave like ordinary Bloch functions along the layers, the conductivity perpendicular to the  $c$  axis will be proportional to  $e^{-E_{\perp}/kT}$  with  $E_{\perp} = E_0 - E_F$  (Fig. 3).  $E_0$ ,  $E_F$  describe the position of the band edge and the position of the Fermi level, respectively. dc transport parallel to the  $c$  axis has to pass through a region where the local band edge is at  $E_{\text{perc}}$ . The conductivity  $\sigma_{\parallel}$  is therefore proportional to  $e^{-E_{\parallel}/kT}$ , with  $E_{\parallel} = E_{\text{perc}} - E_F$  (Fig. 3). By comparison of the two results we obtain in agreement with the experiment [ Eq. (1) ] an anisotropy behaving as  $e^{-\Delta E/kT}$ , where the activation energy  $\Delta E$  is given by  $\Delta E = E_{\text{perc}} - E_0$ .

In the following we shall discuss the dependence of this activation energy on the concentration of stacking faults  $x$  as well as the disorder parameter  $\Delta$ . We have scaled our results for the case of GaSe, i.e., we supposed an unperturbed bandwidth of 1 eV.<sup>1</sup> In Fig. 4, the results for different

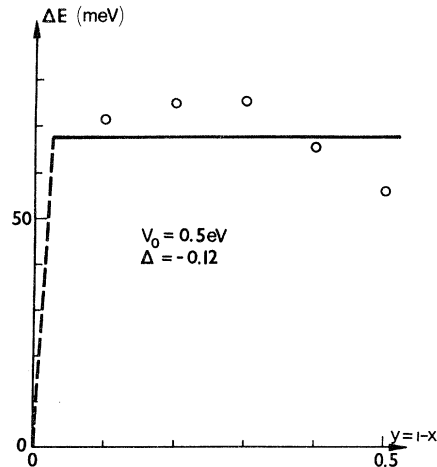


FIG. 4.  $x$  dependence of  $\Delta E$ .

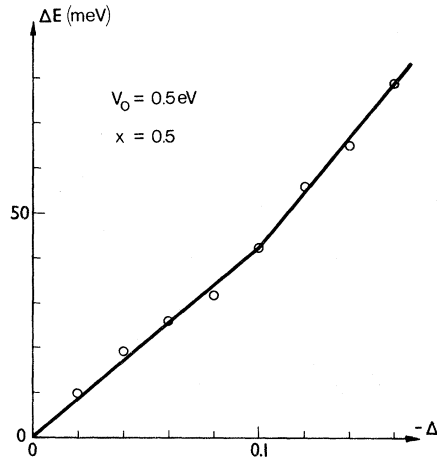


FIG. 5.  $\Delta$  dependence of  $\Delta E$ .

concentrations  $x$  are given. It is seen that the activation energy is essentially constant for  $x > 0.1$ . Unfortunately, the statistical noise prevents an extension of our numerical study to concentrations below  $x = 0.1$ . However, since in a one-dimensional resistor network the largest resistance governs the sample resistivity, we believe that the weak dependence of  $\Delta E$  on the concentration  $x$  remains valid even in the limit of very small stacking fault concentrations.

The dependence on the disorder parameter  $\Delta$  is shown in Fig. 5. The activation energy increases approximately linearly with  $\Delta$ . In the case of GaSe the experimental values for  $\Delta E$  vary from 10 to 100 meV.<sup>1</sup> As according to the previous results the concentration of the stacking faults is not important, at least for concentrations larger than 0.1, we therefore may conclude that

the different stackings found in GaSe can be described by couplings fluctuating in the range of (4–20)%. Relative deviations of more than 10%, however, cannot be explained by a mixture of  $\beta$ -,  $\gamma$ -, and  $\epsilon$ -type stackings alone.<sup>1</sup> Activation energies of more than 50 meV therefore indicate the presence of more serious stacking faults as, e.g.,  $\beta'$  stackings.<sup>4</sup>

#### IV. CONCLUSION

We have shown that the influence of stacking faults on the conductivity along the layer normal can be described in terms of a one-dimensional model. In particular we have discussed the special case of a considerable density of stacking faults. In this case, the electron states extend over a considerable length with nearly constant amplitude. Hopping, therefore, is not governed by the exponential tails of the states as usually assumed. Consequently our model does not lead to variable range hopping at lower temperatures. In this paper we have considered the case of a high concentration of stacking faults with a rather small variation of the interaction between adjacent layers. The opposite limiting case of a small concentration of stacking faults could not be treated numerically because of the statistical noise which accompanies the numerical treatment of this problem. Experimentally the concentration of stacking faults is not yet known. The comparison with the anisotropy of the thermopower might be helpful to distinguish between both cases (see for instance the similar problems for Se).<sup>5</sup>

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