One-dimensional hopping mobility in disordered layered semiconductors: Applications to InSe

A. Khater, M. Balkanski, C. Julien, and M. Weber
Laboratoire de Physique des Solides, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cédex 05, France
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Calculations are presented for a one-dimensional model of electrical transport along the c axis in disordered layered semiconductors, using a multiphonon-assisted hopping mechanism for the electronic carriers between excitons weakly bound to impurities. The excitons are intermediate states. The effect of the stacking disorder involves stochastic field variations, and consequently configurational averages that are calculated for the parallel mobility, which is obtained generally in activated form. The theoretical results are analyzed for InSe and compare favorably with measurements in this compound.

I. INTRODUCTION

The optical and cyclotron resonance properties of layered semiconductors, such as InSe,[1-7] are of interest as this leads to an understanding of their electronic properties. The electrical properties of this material are also directly investigated by carrier mobility experiments[8-16] to determine the specific characteristics which the mechanical anisotropy causes. The remarkable feature of these measurements is that optical and cyclotron resonance data can be interpreted in terms of a three-dimensional model of electronic band structures,[2,3,5-7] with an anisotropy parameter ~ 1 determined from effective masses parallel and perpendicular to the c axis, whereas the transport data are highly anisotropic[13,15,17] for the mobilities, $\mu_\perp$ perpendicular, and $\mu_\parallel$ parallel to c, with $\mu_\perp/\mu_\parallel \sim 10^2$.

Furthermore, the perpendicular mobility variation at low temperatures is $\sim T^{3/2}$, a behavior that is characteristic of charge scattering by ionized impurities, and at higher temperatures is $\sim T^{-\gamma}$ where γ depends on sample preparation.[15] The latter variation is modeled in a number of cases by charge scattering from homopolar optical phonons,[18,19] in these materials. The parallel mobility in contrast varies as $\sim \exp(-E_a/kT)$, where E_a is an activation energy usually associated with a hopping mechanism. This effect is reported by Atakishiev *et al.*,[9] and has been given by other authors[10,16] for InSe. It is also observed in different layered semiconductors,[20-22] suggesting a general behavior due to stacking disorder in these materials.

The anisotropic transport effects are thought to be due to the presence of a high density of stacking faults that inhibit carrier motion parallel to c.[6,7] *Ionized impurities* accumulate at a stacking fault resulting in an *effective Coulomb field* across it, and alternate faults consequently confine the carrier within a few layers. The influence of stacking disorder on the electrical properties of layered semiconductors has been discussed theoretically[20] in terms of one-dimensional disordered chains in the direction of c, where it is concluded that the electronic states close to the band edge are confined to a few layers. In another work[23] it is shown that the phonon-assisted tunneling is a dominant process in the motion of the weakly localized excitons, which confirms their hopping character.

In this paper we present a one-dimensional model for electrical transport parallel to c, using for the electronic carrier a hopping mechanism across the fields of the stacking faults. The intermediate states are treated as the three-dimensional excitons weakly bound to impurities, such that the hopping involves the following process:

$$(i)^{e^-} + (j)\, e^- \rightleftharpoons (i) + (j)^{e^-} \cdot$$

An exciton weakly bound to an impurity at site i loses its electron to another at site j, by an electron multiphonon-assisted hop, with the effective annihilation of an exciton at i and the creation of another at j. The process is reversible, and occurs across the fields of the stacking faults. The conduction due to electron hopping is formulated in terms of the normalized directional probability for the net charge transfer between two such sites. Since the system is disordered the current density is calculated as a configurational average over stochastic distributions for site separations in real space and for energy splittings. We show that the current is linear with externally applied electric fields for relatively small fields, and obtain the temperature activated form for the parallel mobility. The theoretical results are general for any layered semiconductor with stacking disorder. They are analyzed in detail for InSe, and compare favorably with measurements in this material.

II. ELECTRON HOPPING OVER ONE-DIMENSIONAL DISORDER

Consider two impurity sites i and j separated by a distance r_{ij}, with a stacking fault between them. r_{ij} is a random quantity. The transition rate for an electron hop is calculated using the deformation potential approximation for the electron-phonon interaction. Excitonic wave functions are taken from the effective-mass theory, such that the lowest energy states of an electron on the exciton as an intermediate state, are given in the tight-binding formalism over the conduction-band minima eigenstates. The number n of such a basic set varies with the model calculation. An adequate choice[24] is $n = 14$. The transi-

tion rate for an electron phonon-assisted hop can be given[25] in the form

$$U_{ij}=A\,(r_{ij}/a)^{3/2}\exp(-2r_{ij}/a)\{\Delta\varepsilon_{ij}^{0}/[\exp(\beta\Delta\varepsilon_{ij}^{0})-1]\}\ , \tag{1}$$

where a is the Bohr radius of the exciton in the ground state, and $\beta=(kT)^{-1}$. The energy splitting in the hop is

$$\Delta\varepsilon_{ij}^{0}=\varepsilon_{j}^{0}-\varepsilon_{i}^{0}\ , \tag{2}$$

where ε_i^0 and ε_j^0 are the zeroth-order energy levels of the electron on i and j excitons, respectively, in the Coulomb field of the stacking faults. $\Delta\varepsilon_{ij}^0$ is a random quantity for the disordered layered semiconductor. We calculate the factor A in Eq. (2), using the deformation potential due to homopolar optical phonons polarized along the normal to the layers. It can be expressed as

$$A=\frac{\varepsilon^{2}}{\pi\langle\,|\,\Delta\varepsilon_{ij}^{0}\,|^{2}\rangle\rho v^{3}\hbar^{2}}\times\left[\frac{2e^{2}}{3\epsilon_{0}a}\right]^{2}\frac{1}{n}\left[\frac{\pi}{4(m_{\perp}/m_{\parallel}-1)}\right]^{1/2}\ , \tag{3}$$

where ρ and v are the density and transverse speed of sound, respectively, ϵ_0 is the dielectric constant, $m_\parallel$ and $m_\perp$ are the effective electron masses parallel and perpendicular to c, and ε (Ref. 19) is the potential gradient across the van der Waals gap, in the layered material. $\langle\,|\,\Delta\varepsilon_{ij}^{0}\,|^{2}\rangle$ is the variance of the distribution of energy splittings over the ensemble of stacking faults, for which the standard deviation in an ideal crystal with no disorder identifies a single-phonon mode. In one dimension we define a normalized directional probability for the net charge transfer from i to j using (1), to obtain

$$P_{ij}=(U_{ij}-U_{ji})/(U_{ij}+U_{ji})=\tanh(\beta\Delta\varepsilon_{ij}/2)\ . \tag{4}$$

The effect of stacking disorder in the bulk involves configurational averages along c. These are calculated with the use of two distributions, the first $\langle\cdots\rangle_r$ depicts the stochastic probability for the separations in real space between two impurity sites i and j, and the second $\langle\cdots\rangle_{\Delta\varepsilon}$ that for the energy splittings in the hopping processes between the sites. We take the first in the normalized form

$$\langle\cdots\rangle_{r}=(4/\bar{r}^{2})\int r_{ij}\exp(-2r_{ij}/\bar{r})\cdots dr_{ij}\ . \tag{5}$$

This is a modified Poisson distribution which, with no loss of generality, assigns the dominant probability to the mean separation $\langle r_{ij}\rangle=\bar{r}$ between impurity nearest neighbors.

There is no detailed information available as regards the second distribution, usually associated with a single-trap level. We know, however, from photoluminescence measurements at low temperatures that the envelope of the density of states of weakly bound excitons along the layers in the $E\perp c$ polarization shows a Gaussian-like spectrum.[23] The stacking disorder giving rise to this stochastic distribution suggests a similar distribution along the c direction, with a generalized variance. We therefore take the second distribution as the normalized Gaussian:

$$\langle\cdots\rangle_{\Delta\varepsilon}=\frac{1}{\sqrt{2\pi\sigma}}\int_{-\infty}^{-\langle\Delta\varepsilon_{ij}^{0}(\min)\rangle}+\int_{\langle\Delta\varepsilon_{ij}^{0}(\min)\rangle}^{+\infty}\left[\exp\left[-\frac{(\Delta\varepsilon_{ij}^{0})^{2}}{2\sigma^{2}}\right]\cdots d\Delta\varepsilon_{ij}^{0}\right]\ . \tag{6}$$

In this disordered system it is further appropriate to consider a symmetric distribution that yields a net zero current for zero external electric fields. The limits on the integral $\pm\langle\Delta\varepsilon_{ij}^{0}(\min)\rangle$ are finite to depict a significant probability only for nonzero energy splittings over the stacking faults. Furthermore, the limit when $\langle\Delta\varepsilon_{ij}^{0}(\min)\rangle\to 0$ implies that hopping still occurs with dominant contributions from $\Delta\varepsilon_{ij}^{0}=0$ hops. In the complete absence of stacking disorder this limit can be interpreted by taking the standard deviation σ to be the energy of a particular homopolar optical-phonon mode.[19,13]

The total configurational average is now given in general by

$$\langle\cdots\rangle=\langle\langle\cdots\rangle_{r}\rangle_{\Delta\varepsilon}=\langle\langle\cdots\rangle_{\Delta\varepsilon}\rangle_{r}\ , \tag{7}$$

where we have assumed in a first approximation for the disorder that the distributions are independent, and $\Delta\varepsilon_{ij}^0$ is not explicitly a function of r_{ij}.

III. HOPPING MOBILITY

The current density is the configurational average of the net rate of charge hopping. For an independent one-electron model of the nondegenerate electron gas, it is given using (1) and (4)–(7) by

$$j=\langle(e/S_{ij})P_{ij}U_{ij}\rangle\ , \tag{8}$$

where S_{ij} is the area across which the charge transfer occurs in the i to j hop.

In the absence of externally applied electric fields there are equal likelihoods for back and forth hops, and putting (4)–(7) into (8) yields the configurational average of the net hopping current as zero. If the externally applied electric field $E\neq 0$, however, the energy splitting between the excitons at i and j is modified owing to the work done on the electronic charge in going from one site to the other, so that

$$\Delta\varepsilon_{ij}=\Delta\varepsilon_{ij}^{0}+er_{ij}E\equiv\Delta\varepsilon_{ij}^{0}+s\ . \tag{9}$$

For electric fields $E\lesssim 10^{2}$ V cm^{-1} and usual concentrations of impurities, the inequality $er_{ij}E\ll\langle\,|\,\Delta\varepsilon_{ij}^{0}\,|\,\rangle$ can be shown to hold. Putting (9) into (4) we obtain under these conditions the modified probability of the net charge transfer between i and j, in the linearized form

$$P_{ij}(E\neq 0)=P_{ij}(E=0)+[1-P_{ij}^{2}(E=0)](\beta s/2)\ . \tag{10}$$

The first term on the right-hand side of (10) does not contribute to the hopping current, whereas the second one does. It should be clear that (10) is inappropriate for high electric fields as the conductivity becomes field dependent. This can be seen from (9) and (4) in (8), and is in fact experimentally observed in layered semiconductors.[26]

In order to compute A of (3) we should calculate the variance $\langle |\Delta\varepsilon_{ij}|^2\rangle = \langle |\Delta\varepsilon_{ij}^0|^2\rangle$ of the energy splittings in the nonzero limit of $\langle\Delta\varepsilon_{ij}(\min)\rangle$. Using the general form (6) this is

$$\langle |\Delta\varepsilon_{ij}|^2\rangle = \sigma^2 + \langle\Delta\varepsilon_{ij}^0(\min)\rangle^2 . \tag{11}$$

Furthermore, the concentrations N_i and N_j of the impurities yield $\bar{r}$ and $\langle S_{ij}\rangle$, and we take the number of impurities involved in the hopping $(N_iN_j)^{1/2}$ to be a constant with temperature.

The one-dimensional hopping mobility is calculated as a configurational average using (5), (6), (8), and (10). It can be expressed as

$$\mu = \frac{3.14\,Aea^3(N_iN_j)^{1/6}}{(2+K^{1/3}+K^{-1/3})} I(m,\rho_{\min}) , \tag{12}$$

where

$$I(m,\rho_{\min}) = \int_{\rho_{\min}}^{\infty} \left[1-\tanh^2\left[\frac{m\rho}{2}\right]\right] \frac{m\rho e^{-\rho^2}}{e^{m\rho}-1} d\rho . \tag{13}$$

The quantities in (12) and (13) are defined by

$$m = \frac{\sqrt{2}\sigma}{kT}, \quad \rho_{\min} = \frac{\langle\Delta\varepsilon_{ij}^0(\min)\rangle}{\sqrt{2}\sigma}, \quad K = \frac{N_j}{N_i} . \tag{14}$$

noting that $\langle\Delta\varepsilon_{ij}(\min)\rangle \approx \langle\Delta\varepsilon_{ij}^0(\min)\rangle$. It is instructive to study the behavior of the integral $I(m,\rho_{\min})$ in the high- and low-temperature limits, $m \ll 1$, $\rho_{\min} \gtrsim 1$, and $m \gtrsim 1$, $\rho_{\min} \gtrsim 1$, respectively, and this is done in the following section.

For $m\rho_{\min} \ll 1$ and $\rho_{\min} \gtrsim 1$ it is straightforward to show that the integral contributes mainly as

$$I(m,\rho_{\min}) = \int_{\rho_{\min}}^{\infty} e^{-\rho^2} d\rho = \frac{\sqrt{\pi}}{2}[1-\mathrm{erf}(\rho_{\min})] . \tag{15}$$

This implies that the hopping current increases until it saturates at sufficiently high temperatures. For lower temperatures $m\rho_{\min} \gtrsim 1$ we obtain

$$I(m,\rho_{\min}) = \frac{\rho_{\min} e^{-\rho_{\min}^2}}{1+\rho_{\min}/2m - \frac{1}{2}m\rho_{\min}} e^{-2m\rho_{\min}} . \tag{16}$$

This result is of particular interest since it applies for temperatures over which experimental measurements are usually made. In the InSe for example, it applies for temperatures up to 500 K as can be seen from the numerical analysis. Substituting (16) and (14) into (12) yields the one-dimensional hopping mobility as

$$\mu = \frac{3.14\,Aea^3(N_iN_j)^{1/6}}{(2+K^{1/3}+K^{-1/3})} \rho_{\min} e^{-\rho_{\min}^2} \times \frac{e^{-2T_0/T}}{1+[(T_0^2/2\sigma^2)-\frac{1}{2}](T/T_0)} , \tag{17}$$

where

$$T_0 = \langle\Delta\varepsilon_{ij}^0(\min)\rangle/k . \tag{18}$$

The stacking disorder along the direction of c in layered semiconductors is characterized in our model by $T_0 \gtrsim T$ for temperatures of experimental interest. Equation (17) depicts consequently a general activated form with temperature for the parallel mobility $\mu_\parallel$ in these materials, where the exponential dominates the temperature variation. The configurational average of (18) is obtained comparing with experimental measurements as

$$E_a = 2T_0 . \tag{19}$$

The absolute value of the parallel mobility (17) depends on A, and particularly on $\rho_{\min}$, which is obtained from (19)–(14) and σ. The quantity A is calculated using the relevant data for a particular layered semiconductor, and (11) into (3). The quantities $\langle\Delta\varepsilon_{ij}^0(\min)\rangle$ of (18) and the corresponding $\rho_{\min}$ of (14) characterize in the first place the stacking one-dimensional disorder of a layered semiconductor along the c axis, and in the second place strongly influence the strength of the parallel mobility as in (17). In contrast $\mu_\parallel$ is less sensitive to the variation of the impurity concentrations. The parallel mobility of disordered layered semiconductors is determined by their distributions of energy splittings in the fields of stacking faults. No detailed information is available, however, at present as regards such a distribution.

IV. NUMERICAL ANALYSIS AND CONCLUSIONS

The simple theory presented for the hopping current in disordered layered semiconductors gives a good representation of the parallel mobility along the c axis. By comparing the experimentally determined activation energy with theoretical results one can obtain information as regards the strength of this mobility. The small variations of $\mu_\parallel$ from sample to sample are due in this model to the variation of impurity concentrations.

The results presented are applied to InSe, and Eq. (17) is compared to measurements of the parallel mobility in this material.[9] Using (19) we obtain $T_0 = 0.05$ eV, and $\rho_{\min} = 2.52$ for a value $\sigma = 0.014$ eV.[3,15] It follows that (17) applies for temperatures $\lesssim 500$ K. In Fig. 1 a theoretical plot is presented for $\mu_\parallel$ and compared to the experimental data. To obtain absolute values, the quanti-

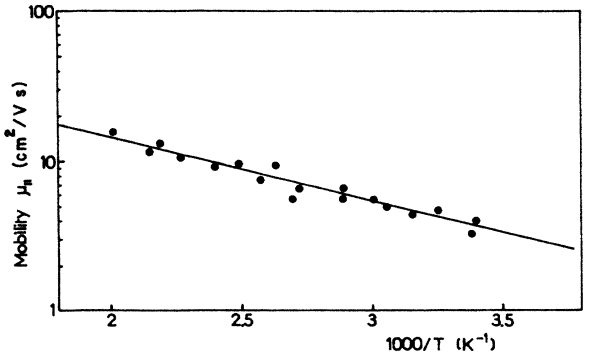

FIG. 1. A theoretical plot is presented for the absolute value of the parallel mobility in InSe as a function of temperature. The dots are experimental measurements from Ref. 9.

ty A of (3) is calculated using the above numerical results, Eq. (12), and the following data: $m_{\perp}=0.13m_0$ and $m_{\parallel}=0.08m_0$,[6,7] $\varepsilon_0=10^5$, $n=14$, $\rho=5.5$ g cm^{-3}, and $v=4\times10^5$ cm sec^{-1}. The value of ε(InSe)$=9.2$ eV/Å is estimated from ε(GaSe)$=6.6$ eV/Å (Ref. 27) and taking g^2(InSe)$=0.06$ (Ref. 15). The mobility is calculated using $N_i=N_j=10^{16}$ cm^{-3} and $K=1$.

In this paper a one-dimensional model for electrical transport is presented in disordered layered semiconductors, using a hopping mechanism for the electronic carrier between three-dimensional excitons as intermediate states weakly bound to impurities. The hopping process is reversible and occurs across the field of the stacking faults. The effect of stacking disorder involves configurational averages that are calculated for the one-dimensional current density and mobility. The activated form and absolute value of the parallel mobility along the c axis are calculated for a disordered layered semiconductor using a Gaussian distribution for energy splittings in the fields of the stacking faults. The results are analyzed for InSe and compare favorably to measurements in this compound.

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