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ON THE EINSTEIN RELATION IN QUANTUM WELL WIRES OF $A_3^{II}B_2^V$ SEMICONDUCTORS

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An attempt is made to investigate the Einstein relation for the diffusivity-mobility ratio of the carriers in quantum well wires of $A_3^{II}B_2^V$ semiconductors, taking n-Cd_3P_2 as an example. On the basis of a newly derived $E - k_z$ dirpersion relation of the carriers, which includes various types of anisotropies in the energy spectrum, it is found that the above ratio increase with increasing electron concentration. In addition, the corresponding results of parabolic semiconductors are also obtained from the expressions derived.

1. *Introduction*

The remarkable developments of fine line lithography and the new epitaxial technologies of molecular beam epitaxy (MBE) and metalogranic chemical vapour deposition (MTCVD) have generated significant possibilities of fabricating new artificial materials. In these materials, the layer dimensions are comparable to the de-Broglie wavelength λ_e and the electrons are confined in 2D representing new characteristics not exhibited in bulk semiconductors. Recently, an alternative structure based on confinement of electrons in a »wire« semiconductor has been proposed

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to investigate the electronic properties of these materials¹⁾. In these 1D synthetic materials, the electron gas is quantized in two transverse directions and the charge carriers can only move in the longitudinal direction$^{1-5)}$. GaAs-AlAs quantum well wires (QWW) have already been proposed by Petroff et al.$^{2)}$. Besides QWW of Bi and $A_3^{II}B_2^{V}$ semiconductors have also been experimentally realized$^{4-5)}$.

The potential use of these new materials for high speed devices makes the knowledge of their transport parameters desirable. Incidentally, it may be noted in this context that the Einstein relation for the diffusivity-mobility ratio of the carriers in semiconductors (hereafter referred to as DMR) is more accurate than any of the individual relations for the diffusivity or the mobility which are considered to be the two most widely used parameters of carrier transport in semiconductors. Since the performance of semiconductor devices at the device terminals and the speed of operation of modern switching semiconductor devices are significantly influenced by the degree of carrier degeneracy, the simplest way of analysing them would be to use the expression for the DMR which in turn enables us to express the above features of the devices made of degenerate semiconductors in terms of carrier concentration$^{6-7)}$. Furthermore, in recent years the connection of the Einstein relation with the velocity auto-correlation function$^{8)}$, its modification due to non-linear charge transport$^{9)}$, the relation of this ratio with the screening of the carriers in semiconductors$^{10)}$ and the different modifications of the DMR for degenerate semiconductors under different physical conditions have been extensively investigated$^{11-18)}$. Nevertheless, it appears from the literature that the DMR in QWW of $A_3^{II}B_2^{V}$ semiconductors has yet to be formulated for the more interesting case which occurs from the consideration of various types of anisotropies in the energy spectrum.

The $A_3^{II}B_2^{V}$ materials are being increasingly used as non-linear optical materials and light emitting diodes$^{19-20)}$. Rowe and Shay$^{21)}$ have demonstrated that the quasi-cubic model$^{22)}$ can be used to explain the observed splitting and symmetry properties of the conduction and valence bands at the zone centre in $\vec{k}$ space of the $A_3^{II}B_2^{V}$ semiconductors. The *s*-like conduction band is singly degenerate and the *p*-like valence band is triply degenerate. The latter splits into three subbands because of spin-orbit and crystal field interactions. Kildal has proposed$^{23-24)}$ an $E - \vec{k}$ dispersion relation for the carriers in the same semiconductor, according to which the conduction band corresponds to a single ellipsoid of revolution at the zone centre in $\vec{k}$-space, together with the assumptions of an isotropic interband momentum-matrix element and isotropic-orbit splitting, respectively.

In what follows we shall generalize the Kildal model by incorporating the anisotropies in the two aforementioned band parameters and formulate the generalized DMR in QWW of $A_3^{II}B_2^{V}$ semiconductors in Sec. 1 of mathematical background. This will make our analysis a generalized since we can also obtain from it the corresponding results for parabolic semiconductors. These special cases are shown in Sec. 2. In Sec. 3 we have suggested an experimental method of determining the DMR in degenerate semiconductors having arbitrary dispersion laws. We have studied the doping dependence in quantum well wires of $A_3^{II}B_2^{V}$ semiconductors, taking n-Cd_3P_2 as an example which is being used in lasers and photodetectors near infrared region.

2. *Theoretical background*

General

The form of the $\vec{k} \cdot \vec{p}$ matrix for $A_3^{II} B_2^{V}$ semiconductors can be written, following Kildal[23], as

$$H = \begin{bmatrix} H_1 & H_2 \\ H_2^+ & H_1 \end{bmatrix} \tag{1}$$

where

$$H_1 = \begin{bmatrix} E_g & P_{\parallel} k_z & 0 & 0 \\ P_{\parallel} k_z & -\left(\delta + \frac{1}{3}\Delta_{\parallel}\right) & \frac{\sqrt{2}}{3}\Delta_{\perp} & 0 \\ 0 & \frac{\sqrt{2}}{3}\Delta_{\perp} & -\frac{2}{3}\Delta_{\parallel} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

$$H_2 = \begin{bmatrix} 0 & 0 & \frac{P_{\perp}}{\sqrt{2}}(k_x - ik_y) & \frac{P_{\perp}}{\sqrt{2}}(k_x + ik_y) \\ 0 & 0 & 0 & 0 \\ -\frac{P_{\perp}}{\sqrt{2}}(k_x - ik_y) & 0 & 0 & 0 \\ \frac{P_{\perp}}{\sqrt{2}}(k_x + ik_y) & 0 & 0 & 0 \end{bmatrix},$$

E_g is the band gap, $P_{\parallel}$ is the momentum-matrix element along *c*-axis, $\Delta_{\parallel}$ is the spin-orbit splitting parameter along *c*-axis, $\vec{k}_z$ is the longitudinal component of the wave-vector along *c*-axis, δ is the crystal-field splitting parameter, $\Delta_{\perp}$ is the spin-orbit splitting parameter in a plane perpendicular to *c*-axis and $P_{\perp}$ is the momentum-matrix element perpendicular to the *c*-axis.

Thus, neglecting the contributions of the higher bands and the free electron energy, the diagonalization of the above matrix leads to the generalized expression of the dispersion relation of the conduction electrons in bulk specimens of $A_3^{II} B_2^{V}$ semiconductors as

$$C(E) = A(E)[k_x^2 + k_y^2] + B(E)k_z^2 \tag{2}$$

where

$$C(E) = E(E + E_g)[(E + E_g)(E + E_g + \Delta_{\parallel}) +$$

$$+ \delta(E + E_g + \frac{2}{3}\Delta_{\parallel}) + \frac{2}{9}(\Delta_{\parallel}^2 - \Delta_{\perp}^2)],$$

E is the energy as counted from the bottom of the conduction band in the absence of any quantization,

$$A(E) = [L_{\perp}(E)/2]\,[(E + E_g)\{(E + E_g + \frac{2}{3}\Delta_{\parallel}) +$$

$$+ \delta(E + E_g + \frac{1}{3}\Delta_{\parallel}) + \frac{1}{9}(\Delta_{\parallel}^2 - \Delta_{\perp}^2)\}],$$

$$L_{\parallel,\perp}(E) \equiv 2\hbar^2 E_g(E_g + \Delta_{\parallel,\perp})\,[2\,m^*_{\parallel,\perp}(E_g + \frac{2}{3}\Delta_{\parallel,\perp})]^{-1},$$

$m^*_{\parallel}$ and $m^*_{\perp}$ are the longitudinal and transverse effective masses of the electron at the edge of the conduction band, respectively, $\hbar = h/2\pi$, h is Planck's constant and

$$B(E) = [L_{\parallel}(E)/2]\,[(E + E_g)(E + E_g + \frac{2}{3}\Delta_{\parallel})].$$

The modified electron energy spectrum in QWW of $A_3^{II} B_2^{V}$ materials can be written following Brum[25] and using (2) as

$$C(E) = A(E)\,[n_1\pi/d_1)^2 + (\pi n_2/d_2)^2] + B(E)\,k_z^2 \tag{3}$$

where $n_1, n_2 = 1, 2, 3, \ldots$, d_1 and d_2 are the dimensions of the rectangular QWW of $A_3^{II} B_2^{V}$ semiconductors.

The use of (3) leads to the expression of the electron concentration per unit length as

$$n_0 = (l_0/\pi) \sum_{n_1=1}^{n_{1max}} \sum_{n_2=1}^{n_{2max}} [\Psi(n_1, n_2, E_F) + \Theta(n_1, n_2, E_F)] \tag{4}$$

where

$$l_0 = 1,\quad \Psi(n_1, n_2, E_F) = [B^{-1}(E_F)\{C(E_F) -$$

$$- A(E_F)\,\pi^2\,\{n_1^2 d_1^{-2} + n_2^2 d_2^{-2}\}\}^{1/2}],$$

$$\Theta(n_1, n_2, E_F) = \sum_{r=1}^{s} 2(k_B T)^{2r}(1 - 2^{1-2r})\,\zeta(2r)\,\frac{d^{2r}}{dE_F^{2r}}\,[\Psi(n_1, n_2, E_F)],$$

k_B is Boltzmann constant, T is temperature, r is the set of real positive integers, E_F is the corresponding Fermi energy and $\zeta(2r)$ is the zeta function of order $2r$. Using the principle of detailed balance, the DMR can be expressed[11] as

$$\frac{D}{\mu} = (n_0/e)\left(\frac{\partial n_0}{\partial E_F}\right)^{-1}. \tag{5}$$

We can combine (4) and (5) to express the same ratio in quantum well wires of $A_3{}^{II}B_2{}^{V}$ semiconductors as

$$\frac{D}{\mu} = l_0 \left(\frac{n_0}{e\pi}\right) \sum_{n_1=1}^{n_{1max}} \sum_{n_2=1}^{n_{2max}} [Z\Psi(n_1, n_2, E_F) + Z\Theta(n_1, n_2, E_F)] \tag{6}$$

where

$$Z = \frac{\partial}{\partial E_F}.$$

Special cases

(1) Under the substitutions $\delta = 0$, $\Delta_{\parallel} = \Delta_{\perp} = \Delta$ (the isotropic spin-orbit splitting parameter) and $m^*_{\parallel} = m^*_{\perp} = m^*$ (the isotropic effective electron mass at the edge of the conduction band) (2) assumes the form

$$\frac{\hbar^2 k^2}{2m^*} = \omega(E),\quad \omega(E) \equiv \frac{E(E+E_g)(E+E_g+\Delta)\left(E_g + \frac{2}{3}\Delta\right)}{E_g(E_g+\Delta)\left(E+E_g+\frac{2}{3}\Delta\right)} \tag{7}$$

which is the standard dispersion relation of the conduction electrons of Kane-type semiconductors and is known as three-band Kane model$^{26)}$. Thus using the above mentioned substitutions, the general forms of the electron statistics and the DMR for quantum well wires of semiconductors whose energy-band structures are defined by three-band Kane model will, respectively, be given by (4) and (6) where

$$\Psi(n_1, n_2, E_F) = [\omega(E_F) - \frac{\hbar^2\pi^2}{2m^*}\{n_1^2 d_1^{-2} + n_2^2 d_2^{-2}\}]$$

and

$$l_0 = \sqrt{2m^*}/\hbar.$$

It may be noted that above expressions are quite general for Kane-type semiconductors and should be used as such where $\Delta \simeq E_g$ (e. g. in InAs).
(2) For $\Delta \to \infty$, (7) gets simplified into the form

$$E(1 + \alpha_0 E) = \frac{\hbar^2 k^2}{2m^*},\quad \alpha_0 \equiv 1/E_g \tag{8}$$

which is well-known 2-band Kane model$^{11)}$. Thus under the condition $\Delta \to \infty$ the general forms of the electron statistics and the DMR according to two-band Kane model will, respectively, be given by (4) and (6) where

$$\Psi(n_1, n_2, E_F) = [E_F(1 + \alpha_0 E_F) - \frac{\hbar^2\pi^2}{2m^*}(n_1^2 d_1^{-2} + n_2^2 d_2^{-2})]^{1/2}$$

and

$$l_0 = \sqrt{2m^*}/\hbar.$$

(3) It is also interesting to note that for $\alpha_0 \to 0$, i. e. for parabolic semiconductors, (4) and (6) get further simplified as

$$n_0 = d_0 \sum_{n_1=1}^{n_{1max}} \sum_{n_2=1}^{n_{2max}} F_{-1/2}(\eta) \tag{9}$$

and

$$\frac{D}{\mu} = \frac{k_B T}{e} [\sum_{n_1=1}^{n_{1max}} \sum_{n_2=1}^{n_{2max}} F_{-1/2}(\eta)] [\sum_{n_1=1}^{n_{1max}} \sum_{n_2=1}^{n_{2max}} F_{-3/2}(\eta)]^{-1} \tag{10}$$

where

$$d_0 = (\sqrt{2m^* k_B T}/2\hbar \sqrt{\pi}), \qquad \eta = (k_B T)^{-1} [E_F - a(n_1, n_2)],$$

$$a(n_1, n_2) = \frac{\hbar^2}{2m^*} \left[\frac{n_1^2 \pi^2}{d_1^2} + \frac{n_2^2 \pi^2}{d_2^2}\right]$$

and $F_j(\eta)$ is the Fermi-Dirac integral of order j as defined by Blakemore[27].

Suggested experimental procedure for determining DMR

It is well-known that the thermoelectric power of the electrons in the presence of a classically large magnetic field is independent of scattering mechanisms[28-29]. For QWW the same power can be expressed, following Tsidilkovski[28], as

$$G_\infty = H_0/e\, n_0 \tag{11a}$$

where H_0 is the entropy per unit length.

Eq. (11a) for 1D electron motion can be expressed as

$$G_\infty = (\pi^2 k_B^2 T/3n_0) \left(\frac{\partial n_0}{\partial E_F}\right). \tag{11b}$$

Thus combining (11a) and (11b) we get

$$\frac{D}{\mu} = \pi^2 k_B^2 T/3e^2 G_\infty. \tag{11c}$$

Since the classically large magnetic field does not change the density-of-states function therefore the DMR in the presence of a classically large magnetic field will be equal to the same ratio in the absence of that field[11]. Thus we can experimentally determine DMR for any arbitrary dispersion relation by knowing G_∞, which is an easily measurable experimental parameter.

3. *Results and discussion*

Using (4) and (6) together with the parameters[5)] $d_1 = 30$ nm, $d_2 = 50$ nm, $m^*_{\|} = 0.03\, m_0$, $m^*_{\perp} = 0.05\, m_0$, $\Delta_{\|} = 0.22$ eV, $\Delta_{\perp} = 0.28$ eV, $T = 4.2$ K, $\delta = 0.08$ eV and $E_g = 0.58$ eV as appropriate for n-Cd_3P_2 we have plotted the Fermi energy as a function of electron concentration per unit length in QWW of Cd_3P_2 as shown in plot a of Fig. 1 in which the same dependence is also plotted by taking the crystal field parameter as zero. In the same figure the plots corresponding to degenerate three band Kane model, degenerate two-band Kane model and that for a degenerate parabolic energy bands are also shown by taking $\Delta = 0.25$ eV and $m^* = 0.04\, m_0$ for the purpose of numerical comparisons. In Fig. 2 we have plotted G_∞ as a function of electron concentration per unit length by using the corresponding experimental values as given in Ref. 5. In Fig. 3 we have plotted the DMR versus n_0 in quantum well wires of Cd_3P_2 in which the dotted variation b also exhibits the

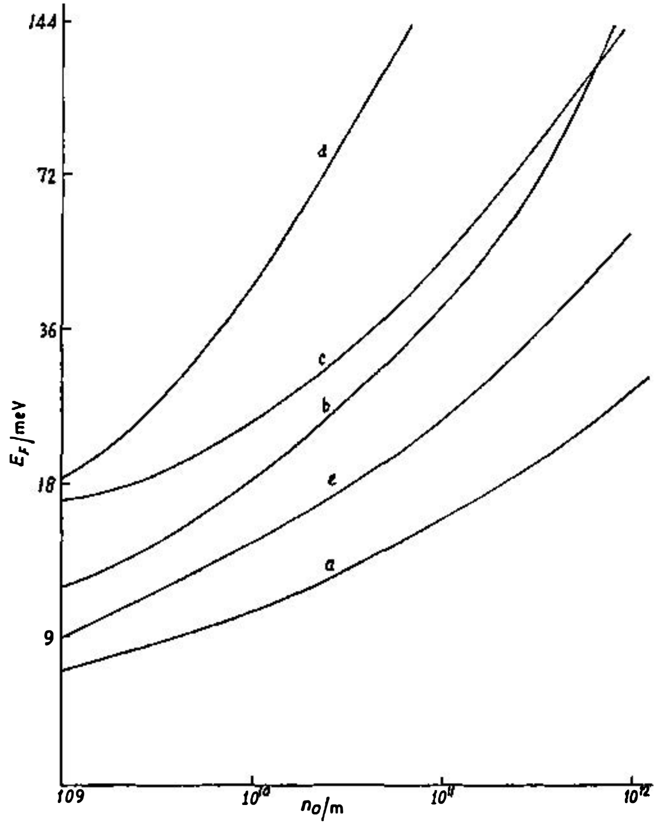

Fig. 1. Plot of the Fermi energy as a function of the electron concentration per unit length in quantum well wires of n-Cd_3P_2 at 4.2 K by using (a) the proposed dispersion relation, (b) the isotropic three-band Kane model, (c) the isotropic two-band Kane model and (d) the isotropic parabolic energy bands. Curve e corresponds to $\delta = 0$.

same dependence and is plotted by using Eq. (11c) together with the help of Fig. 2. Besides, the other simplified limiting cases have further been demonstrated in Fig. 3.

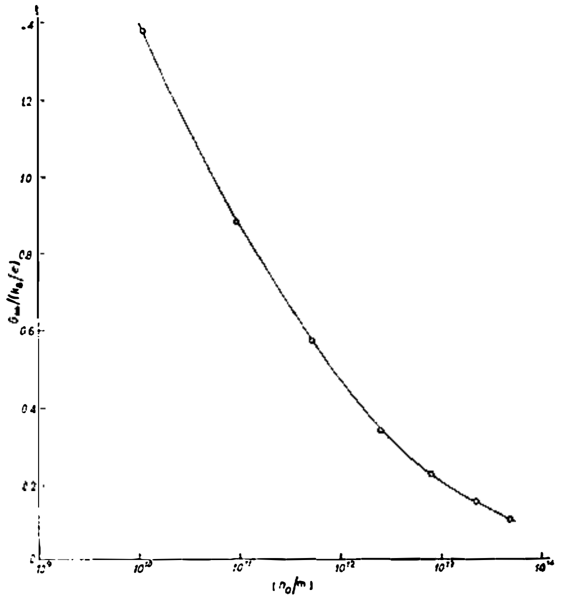

Fig. 2. Plot of the thermoelectric power of the electrons in the presence of a classically large magnetic field in quantum well wires of n-Cd$_3$P$_2$ as a function of the electron concentration per unit length by using the corresponding experimental values as given in Ref. 5.

It is observed from the experimental plot of Fig. 2 that G_∞ decreases with increasing electron concentration. From Eq. (11c) it appears that DMR is inversely proportional to G_∞ at a constant temperature. Therefore we conclude that DMR must increase with increasing carrier degeneracy. From Fig. 3 we note that the dependence of DMR on electron concentration is in accordance with our conclusion. It is worth remarking that the tetragonal crystal field affects the DMR quite significantly in QWW of $A_3^{II}B_2^{V}$ semiconductors for relatively large values of the electron concentration. Furthermore, for a fixed value of the electron concentration, the DMR is smaller as compared to that in the absence of crystalline field effects in the whole range of concentrations considered. Though DMR increases non-linearly with carrier degeneracy in various other limiting cases, the rates of increases are different from that in the proposed band model. The classical value of DMR is k_BT/e and is equal to 0.36 mV at 4.2 K. This is, therefore, not shown in Fig. 3 as it would be senseless in such figure.

In recent years, the mobility of the electrons in QWW of small-gap semiconductors has been extensively investigated but the diffusion constant (a very important device parameter which cannot be easily experimentally determined) of the such 1D electron gases has relatively been less studied. Thus the theoretical results of our paper will be useful in determining the diffusion constant even for QWW of parabolic semiconductors. The general features of the effects of carrier degeneracy on the DMR in QWW as discussed here would also be valid for most of the

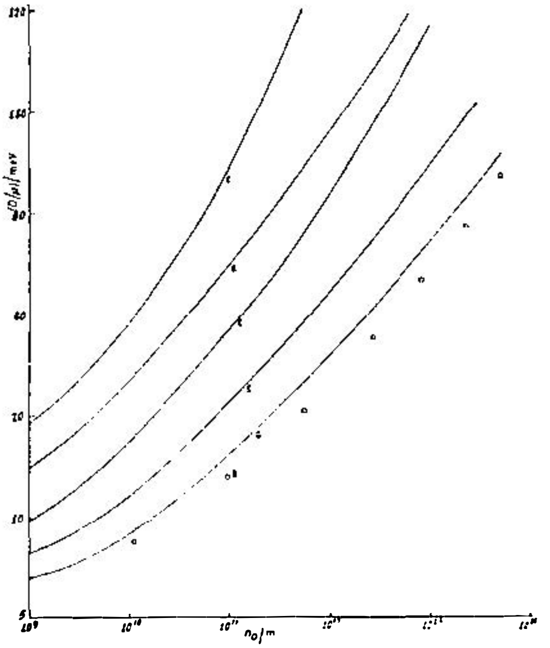

Fig. 3. Plot of the DMR as a function of the electron concentration per unit length in quantum well wires of n-Cd_3P_2 at 4.2 K by using (a) the proposed dispersion relation, (b) the experimental values of the thermoelectric powers of the electrons in the presence of a classically large magnetic field (c) the isotropic 3-band Kane model, (d) the isotropic two-band Kane model and (e) the isotropic parabolic energy bands. Curve f corresponds to $\delta = 0$.

1D systems on small-gap semiconductors since these semiconductors have non-parabolic energy bands obeying Kane's dispersion law whereas the present analysis is based on generalized Kane's theory. We wish to note that the basic purpose of the present paper is not solely to investigate the DMR in QWW of $A_3^{II}B_2^{V}$ semiconductors but also to formulate the generalized carrier statistics by using the various types of band anisotropies in the energy spectrum since the various transport phenomena and the derivation of the expressions for many physical parameters of 1D semiconductors devices are based on the carrier statistics in such devices.

It may be stated that if the direction of free motion of the electrons is taken as either k_x or k_y and not as k_z as assumed in the present work, the DMR would be different analytically. Nevertheless, the arbitrary choice of the direction of free motion would not result in a change of the basic qualitative feature of the DMR in QWW of $A_3^{II}B_2^{V}$ semiconductors. Finally, it may be remarked that though the many-body effects, the hot-electron effects and the formation of band tails have been neglected in the theoretical formulation, the simplified infinitely deep rectangular potential well approximation exhibits the basic qualitative features of the DMR in quantum well wires of $A_3^{II}B_2^{V}$ semiconductors and the agreement between the theory and the suggested experimental method of determination of the same ratio becomes rather significant in spite of the above simplifications.

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O EINSTEINOVOJ RELACIJI U KVANTNO-JAMSKIM ŽICAMA $A_3^{II} B_2^{V}$ POLUVODIČA

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Razmatrana je Einsteinova relacija za omjer difuzivnosti i pokretljivosti nosilaca naboja u kvantno-jamskim žicama $A_3^{II} B_2^{V}$ poluvodiča uzevši n-Cd_3P_2 kao primjer. Na osnovu nedavno izvedene $E - k_z$ disperzione relacije za nosioce naboja a koja uključuje razne anizotropije u energetskom spektru, nađeno je da gornji omjer raste porastom koncentracije elektrona.