Anomalous low temperature ambipolar diffusion and Einstein relation

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Regular Einstein relation, connecting the coefficient of ambipolar diffusion and the Dember field with mobilities, is generalized for the case of interacting electron-hole plasma. The calculations are presented for a non-degenerate plasma injected by light in semiconductors of silicon and germanium type. The Debye-Huckel correlation and the Wigner-Seitz exchange terms are considered. The corrections to the mobilities of carriers due to difference between average and acting electric fields within the electron-hole plasma is taken into account. The deviation of the generalized relation from the regular Einstein relation is pronounced at low temperatures and can explain anomaly of the coefficient of ambipolar diffusion, recently discovered experimentally.

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Introduction

The Einstein relation for electrons\(^1\) \(n Ud\mu/dn = eD\) connects mobility \(U\) with diffusion coefficient \(D\) by the thermodynamic function \(d\mu/dn\) and electron charge \(e\). Here \(\mu\) is chemical potential, \(n\) is electron density. For the case of the Boltzmann gas of non-interacting electrons, where \(d\mu/dn = kT/n\), one gets a regular form of the Einstein relation, presented by Einstein\(^2\) and von Smoluchowsky\(^3\) for the Brownian particles. Here \(kT\) is the temperature in energy units. However, the Einstein relation can be used in a general case of interacting particles\(^4\).

The focus of this paper is the ambipolar diffusivity under condition that interaction between electrons and holes is substantial. I have been initiated by the paper of Hui Zhao\(^5\) who has measured the coefficient of the ambipolar diffusivity (CAD) by optical method in silicon-on-insulator (SOI) structure with 750 nm silicon layer. The doping density is \(10^{15}\) cm\(^{-3}\) while the density \(n\) of electron-hole pairs excited by light is between \((0.5 - 3) \times 10^{17}\) cm\(^{-3}\). The temperature is in the range \(90K - 400K\).

The regular Einstein relation for the CAD in non-degenerate and non-interacting electron-hole plasma has a form

\[
D_a = \frac{2kT}{e} \frac{U_pU_n}{U_p + U_n},
\]

where \(U_n, U_p\) are mobilities of electrons and holes respectively. The CAD observed in Ref.\(^5\) approximately follows Eq.\(^1\) at \(400K > T > 300K\). At lower temperatures the CAD goes down and deviates from the Eq.\(^1\) approximately 7 times at \(T = 90K\). The mobilities were taken from experiments with a pure bulk silicon. Authors explained this anomalous behavior as a result of uncontrolled defects that are absent in a bulk silicon.

I propose here alternative and more universal intrinsic explanation of the low temperature anomaly. This explanation is based upon a novel form of Einstein’s fundamental relation for the CAD, that takes into account interaction between excited carriers.

Under conditions of the experiment the electron-hole plasma can be considered as a non-degenerate. On the other hand, the classical correlation energy per particle \(\sim e^2\alpha^{1/3}/\kappa\) is of the order of 200K. Here \(\kappa\) is dielectric constant. Thus, in the region of the observed anomaly the interaction energy becomes of the order of temperature.

The paper is organized as follows. First the novel form of the fundamental Einstein relation connecting the CAD and the Dember field with mobilities of electrons and holes is derived. The relation contains the derivatives of the Helmholtz energy density (HED) of the interacting plasma with respect to particle densities. The HED is calculated taken into account correlation and exchange between particles. Then the corrections to the mobilities due to deviation of acting electric field from the applied field are considered. Finally the theoretical results are compared with the experimental data.

Einstein relation for ambipolar diffusivity. Thermodynamics approach

Silicon is an example of semiconductor with a long recombination time of interband excitation. Assume that this system is in the thermodynamic equilibrium with respect to all relevant parameters except the total numbers of electrons and holes. To derive the Einstein relation I use here the same method as in Ref.\(^4\). The difference is that excited electrons and holes have two independent electrochemical potentials \(\Phi^a\) and \(\Phi^p\) respectively. The Helmholtz energy has a form

\[
F = \int f(n,p)d^3r + \int e(p(r) - n(r))\psi d^3r - \Phi^p \int p(r)d^3r - \Phi^n \int n(r)d^3r.
\]

Here \(n\) and \(p\) are electron and hole densities. Function \(f(n,p)\) is the HED of the almost neutral and microscopically homogenous electron-hole plasma, the function \(\psi(r)\) is a potential of a static electric field.

Using conditions $\delta F/\delta p = 0$ and $\delta F/\delta n = 0$ one gets
\[ \Phi^p = \frac{\partial f(n,p)}{\partial p} + e\psi \] (3)
and
\[ \Phi^n = \frac{\partial f(n,p)}{\partial n} - e\psi. \] (4)

It follows from the general principles of statistical physics that in the state of equilibrium both $\Phi^p, \Phi^n$ should be constant along the system. Exploring Einstein’s idea that electric field is equivalent to a certain density gradient one can write the fluxes of holes and electrons as
\[ q_p = -\frac{\sigma_p}{e^2} \nabla \Phi^p, \quad q_n = -\frac{\sigma_n}{e^2} \nabla \Phi^n, \] (5)
where $\sigma_p$ and $\sigma_n$ are conductivities of holes and electrons respectively. Then the fluxes are
\[ q_p = \frac{\sigma_p}{e} E - \frac{\sigma_p}{e^2} \left( \frac{\partial^2 f}{\partial p^2} \nabla n + \frac{\partial^2 f}{\partial p \partial n} \nabla p \right) \] (6)
and
\[ q_n = -\frac{\sigma_n}{e} E - \frac{\sigma_n}{e^2} \left( \frac{\partial^2 f}{\partial n^2} \nabla n + \frac{\partial^2 f}{\partial n \partial p} \nabla p \right). \] (7)

Note that separation of the conductivities of electrons and holes are possible only if their mutual scattering is small. We assume here that the mobilities of the carriers are controlled by the lattice scattering. But even in this case the above expressions predict a drag effect due to the interaction terms in the HED. The flux of holes is proportional to gradient of electron density and to gradient of hole density. The same is true for the flux of electrons. For example, if electric field is zero and gradient of electron density is zero, there is an electron flux proportional to a gradient of hole density.

The ambipolar diffusion is measured under condition that electrical circuit is open. Then the total electric current $j$ is zero and $q_p = q_n$. Taking into account the continuity equation
\[ e \partial (p - n)/\partial t + \text{div} j = 0. \] (8)
one finds that since electron and holes are excited by light in equal amounts the system is neutral everywhere. Then $n(r) = p(r)$ and $\nabla n = \nabla p$. A small separation of charges at the boundaries of the sample appears due to a difference of diffusion coefficients of electrons and holes. This difference is compensated by an electric field called the Dember field. Nevertheless, the electron-hole plasma in the bulk of the sample is neutral.

The expressions for fluxes can be written in a form
\[ q_p = \frac{\sigma_p}{e} E - D_p \nabla p \] (9)
and
\[ q_n = -\frac{\sigma_n}{e} E - D_n \nabla n. \] (10)

It follows from Eqs. (6–9, 10) that diffusion coefficients of electrons and holes $D_n$ and $D_p$ are connected with corresponding mobilities $U_n, U_p$ by the relations
\[ D_n = \frac{\delta^2 f}{\delta n^2} n U_n/e \] (11)
and
\[ D_p = \frac{\delta^2 f}{\delta p^2} n U_p/e. \] (12)

Eqs. (11, 12) give a novel form of the Einstein relation that is valid in the case of interacting plasma.

The mixed partial derivatives in these equations describe the drag effect.

Using Eqs. (9, 10) and condition $q_p = q_n$ one gets expression for the Dember field in terms of $D_n, D_p$
\[ E_D = \frac{e}{\sigma_p + \sigma_n} \frac{(D_p - D_n)}{\nabla n}. \] (13)

This regular form becomes more complicated if $D_n$ and $D_p$ are expressed through mobilities $U_n$ and $U_p$ using Eqs. (11, 12). Then
\[ E_D = \left[ e (U_n + U_p) \right]^{-1} \left( \frac{\delta^2 f}{\delta n^2} U_n - \frac{\partial^2 f}{\partial p^2} U_p \right. \]
\[ + \left. \frac{\partial f}{\partial n \partial p} (U_n - U_p) \right) \nabla n. \] (14)

Due to the interaction of carriers the Dember field is not necessarily proportional to the difference of mobilities $U_n - U_p$.

Substituting Eq. (15) into Eqs. (9, 10) one gets
\[ q_n = q_p = -D_n \nabla n, \] (15)
where the CAD
\[ D_a = \frac{D_n U_p + D_p U_n}{U_p + U_n}. \] (16)

Using Eqs. (11, 12) we get the generalized Einstein relation for the CAD
\[ D_a = \frac{2kT}{e} \frac{U_p U_n}{U_p + U_n} Q(n, T), \] (17)
where
\[ Q(n, T) = \frac{n}{2kT} \left( \frac{\delta^2 f}{\delta n^2} + \frac{\delta^2 f}{\partial p^2} + \frac{2 \delta^2 f}{\partial n \partial p} \right) \] (18)
is a ratio of the coefficients of ambipolar diffusivity calculated with and without interaction (cp Eq. (17) with Eq. (11)).

It is important to put $n = p$ after calculation of the second partial derivatives in Eqs. (11, 12, 13, 18).
HED of semiconductors with band structure of Si and Ge

Analytical calculations of the HED of interacting carriers are possible in the framework of perturbation theory only. One should keep in mind, however, that the region of applicability of these calculations does not cover all temperature range of the experiment.

The HED can be written in a form \( J = J_{id} + J_s \), where the first term describes the ideal gas, while the second one takes into account interaction. The non-interacting carriers are independent and \( J_{id} = J_{id}^0(p) + J_{id}^s(n) \). Since only the second derivatives of the HED are necessary, one can write \( J_{id}(p) = p k T (1 + \ln p) \) and \( J_{id}(n) = n k T (1 + \ln n) \).

The largest interaction term for the non-degenerate plasma describes correlation effect. It was calculated by Debye and Huckel in a form

\[
J_c(n + p) = -(2 e^3 / 3 \kappa^{3/2}) \sqrt{\pi / k T} (n + p)^{3/2}.
\]  
(19)

This term is independent of the spectra of electrons and holes. In our approximation this is the only term that has non-zero \( \partial^2 J / (\partial n \partial p) \) and contributes to the drag effect (See Eqs. (62)).

I also take into account the exchange interaction between electrons in each ellipsoid, between heavy holes and between light holes. This interaction term has a higher power of \( T \) in the denominator of the HED than the correlation term. The thermodynamic potential density \( \Omega(\mu, T) \) for this interaction can be written in a form of the Wigner-Seitz integral (See \[7\])

\[
\Omega_{ex} = -4 \pi e^2 \int \frac{\mu_p n_p d^3p_1 d^3p_2}{(p_1 - p_2)^{2}} (2\pi)^6,
\]  
(20)

where \( n_p \) is the Fermi function that has the Boltzmann form in this case. To find the HED one should express chemical potentials through the density of carriers.

For a conduction band consisting of \( g \) equivalent ellipsoids of rotation one gets

\[
f_{ex}(n) = -\frac{m^2 e^2 h^2 I(a)}{4 \sqrt{\pi} g m_\perp k T},
\]  
(21)

where masses \( m_\perp \) and \( m_\parallel \) are perpendicular and parallel to the rotation axis of an ellipsoid, \( a = m_\parallel / m_\perp \). At \( a > 1 \)

\[
I(a) = \frac{2 \sqrt{\pi} \arctan(\sqrt{a - 1})}{\sqrt{a - 1}}.
\]  
(22)

For a parabolic valence band with light hole \( m_l \) and heavy hole \( m_h \)

\[
f_{ex}(p) = -\frac{\pi e^2 h^2 p^2 (m_h^2 + m_l^2)}{2 \kappa k T (m_h^{3/2} + m_l^{3/2})^2}.
\]  
(23)

My final result for corrections to a regular Einstein relation reads

\[
Q(n, T) = 1 - \frac{e^3 \sqrt{\pi} n}{2 \kappa^{3/2} (k T)^{3/2}} - \frac{e^2 h^2 n I(a)}{4 \sqrt{\pi} \kappa m_\perp g (k T)^2} - \frac{\pi e^2 h^2 n (m_h^2 + m_l^2)}{2 \kappa (k T)^2 (m_h^{3/2} + m_l^{3/2})^2}.
\]  
(24)

The Dember field in terms of mobilities has a form

\[
E_D = \frac{1}{(e U_n + e U_p)} \left( \frac{k T}{n} + \frac{e^3 \sqrt{\pi}}{\kappa^{3/2} 2 k T n} \right) (U_p - U_n) - \frac{\pi e^2 h^2 (m_h^2 + m_l^2) U_p}{\kappa k T (m_h^{3/2} + m_l^{3/2})^2} + \frac{e^2 h^2 I(a) U_n}{2 \sqrt{\pi} g m_\perp k T} \right) \nabla n.
\]  
(25)

Mobility of carriers in a plasma

It is assumed above that mobilities of the carriers are controlled by the lattice scattering. But even in this case there are important corrections to these mobilities due to the interaction of electrons and holes. Each carrier is surrounded by a screening atmosphere of the opposite sign. This atmosphere is polarized by an applied electric field. The field of this polarization is opposite to the applied field so that the effective field acting on the carrier is less than applied field. It can be interpreted as a decrease of the mobility. The theory of this effect was created by Debye, Huckel, and Ousager (See Ref. \[3\]). The resulting changes of the mobilities are

\[
S(n, T) = \Delta U_n / U_n = \Delta U_p / U_p = -\frac{\sqrt{2\pi} e^3 n^{1/2}}{3 (1 + \sqrt{0.5}) \kappa^{3/2} (k T)^{3/2}}.
\]  
(26)

Coming back to the Einstein relation Eq. (17), one should note that if the mobilities \( U_n, U_p \) are measured in the presence of plasma, the above corrections are irrelevant because the experimental values \( U_n, U_p \) contain them. However, if the mobilities are known from experiments without light excitation, as in the case of Ref. \[3\], the Einstein relation Eq. (17) takes a form

\[
D_n = \frac{2 T}{e} \frac{U_p U_n}{U_p + U_n} P(n, T),
\]  
(27)

where \( P(n, T) = Q(n, T) + S(n, T) \). One can see that this change increases the numerical factor in the second term of \( Q \), originated from correlation, by 1.39.

Discussion and Conclusion

Now I discuss the low temperature anomaly of the CAD in Si. Function \( P(n, T) \) is shown in Fig.1 in a proper temperature range. The comparison of the first approximation (correlation) with the second one (exchange) shows that the perturbation theory looks reasonable at \( T \geq 150K \) and at \( n_0 = 1 \).
To estimate CAD as a function of $T$ one should know mobilities $U_n$ and $U_p$. The experimental and theoretical data of Ref.\cite{9} show that in silicon $U_p/U_n \approx 0.25$, at $T \approx 200K$. Then $U_pU_n/(U_p + U_n) \approx U_p$. The hole mobility in the pure silicon is due to the phonon scattering and it depends on temperature as $T^{-2.2}$ in all temperature range considered. The deviation from a usual law $T^{-1.5}$ is due to the warping of the top of the valence band. The mobility of doped silicon with the hole density $2 \times 10^{17} cm^{-3}$ has $T^{-1.5}$ dependence\cite{3} at $T > 180K$ that may be interpreted as a phonon scattering but with the warping smeared by the doping. A pure silicon is considered here, and $T^{-2.2}$ mobility dependence is used.

The expression $D_a = P(T)U_pT$ with $U_p = RT^{-2.2}$ is used to get T-dependence of $D_a$ that follows from the above theory. To make comparison with experimental result easier the factor $R$ is chosen such that $D_a = 20 cm^2/sec$ in the maximum, similar to the experimental data of Ref.\cite{3}. The theoretical result is shown in Fig. 2.

Since the HED is calculated using perturbation theory, the discussion of the low temperature behavior might be doubtful, and the most important argument is position of the maximum of CAD. Clearly the way factor $R$ is chosen has no effect on the maximum position. Theoretical position of maximum is 230K, which is close to the experimental position that has some uncertainty because of the large error bars. I think this similarity is a strong argument in favor of the proposed explanation.

In the range $T > 150K$ the theoretical curve is similar to experimental points of Ref.\cite{5}. At lower $T$ theoretical values become negative. This definitely means collapse of the perturbation theory, because negative CAD leads to an absolute instability of a neutral plasma\cite{4}. It is intriguing that just near this temperature the character of experimental data changes: CAD becomes independent of both $T$ and $n$. This might be a manifestation of a new phase. The speculations about this phase are outside the scope of this paper. I would only mention that amount of excitons at these temperatures, as given by the Saha equation, is negligible but the Saha equation is not reliable for the case of non-ideal plasma. It is known also that the phase of exciton gas-liquid coexistence corresponds to lower temperature at these densities\cite{10}.

Finally, I proposed an explanation of the low temperature anomaly of the CAD based upon the Einstein relation for interacting carriers. The applicability of the theory is limited at low enough temperatures because the calculation of the HED is perturbational. Using fundamental thermodynamics relations Eqs.\cite{15,17,18} one could restore unknown thermodynamic functions of the non-ideal plasma at low temperatures by measuring mobilities, CAD, and the Dember field.

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