Nature of the dislocation charge in ZnSe

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A physical model is proposed to explain the experimentally observed anomalously large electric charges of moving dislocations in II-VI semiconductors. The model is based on the idea that broken bonds in the core of a dislocation are filled with electrons from point centers swept through by the dislocation during its motion. The theoretical predictions are compared with the experimental data for ZnSe.

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INTRODUCTION

The presence of electric charges at dislocations has been detected experimentally in many II-VI compounds: ZnS,[1,2] ZnSe,[1,2] CdS,[3,4] and CdSe.[5] A surprising feature is the very high linear density q of such charges, reaching one electronic charge per interatomic distance. The following interesting physical phenomena are associated with the motion of such strongly charged dislocations: the photoplastic effect,[6,7] deformation-induced luminescence,[8,9] influence of electrical boundary conditions on plastic deformation processes,[10] electroplastic effect,[11,12] and influence of dislocation motion on conduction current and photocurrent.[13] However, in spite of the importance of the nature of such high dislocation charges in these physical phenomena, the magnitude of the charge is accepted—with some exceptions[14,15]—as known simply as an experimental fact without interpretation. Oel'g'yan and Petren-
kof et al. used the results of an experimental investigation of the influence of the magnitude of the dislocation charge \( \varphi \) to put forward the hypothesis that \( \varphi \) might be affected by the exchange of electrons between a dislocation and point defects swept through by the dislocation during its motion.

Zaretskii et al. investigated the charges carried by dislocations of various types in CZS and demonstrated that only dislocations with broken bonds in their cores are charged. The present paper is devoted entirely to the nature of dislocation charges in CZS. In the first part of the paper, we shall put forward a physical model of the formation of dislocation charges and, in the second part, we shall compare the predictions deduced from this model with the experimental results.

**Physical Model**

It follows from the published results\(^1\)-\(^8\) that, among dislocations in II-VI compounds, only those are charged which have broken bonds in their cores. Therefore, the presence of such bonds will be regarded as the cause of the appearance of electric charges. As demonstrated by Read\(^,8\)-\(^11\) and the presence of broken bonds in a dislocation core results in the capture of electrons by these bonds, produces a dislocation energy level \( E_D \) in the forbidden band of a semiconductor, and generates electric charges along the dislocation line. The validity of these ideas is now supported by an enormous amount of experimental material obtained in investigations of elemental materials.

The electron occupancy of a dislocation level is governed by the equilibrium Fermi distribution

\[
\psi = \left( 1 + \exp \left( \frac{E_D - \mu}{kT} \right) \right)^{-1},
\]

where \( \psi \) is the occupancy, \( \alpha \) is the distance between the broken bonds (equal to the lattice constant), and \( I \) is the distance between the electrons captured by the bonds.

The Coulomb repulsion between electrons in the dislocation level \( E_D \) causes this level to rise with the electron occupancy so that it very rapidly reaches the chemical potential \( \mu \) and then captures no further electrons. This behavior is responsible for the small experimental values of the occupancy \( \psi \) near 0.1 of dislocations at rest.

However, in the case of a moving dislocation, we cannot calculate \( \psi \) using the equilibrium distribution function (1). One of the reasons for this is as will be shown in Appendix II—that the time is too short for the electrons localized at point defects to reach thermal equilibrium with the conduction band when a charged dislocation passes nearby. Consequently, the occupancy of energy levels near a dislocation (including the level \( E_D \)) is no longer governed by the thermal equilibrium conditions and we can find the distribution of electrons between the various energy levels only by solving the kinetic equations describing electron exchange between them.

In the coordinate system (Fig. 1) linked to a dislocation moving at a constant velocity \( v_D \), these equations are independent of time:

\[
\begin{align*}
P_{\text{in}} - P_{\text{out}} &= \sum_{E_L} \int \int dE_L d\varphi (1 - \exp(-E_L/kT)) \exp \left( \frac{E_L - \mu}{kT} \right) \\
- \psi(E_D) &= \int \int dE_L d\varphi \left[ E_L - \mu \right] \exp \left( \frac{E_L - \mu}{kT} \right) \}
\end{align*}
\]

where \( x \) is the coordinate along the direction of motion of the dislocation; \( \gamma \) is the impact parameter (Fig. 1); \( \omega_{st} \) is the attempt frequency of transitions between a local center of energy \( E_D(x, y) \) and a dislocation level; \( N_L \) and \( n_{st}(x, y) \) are, respectively, the concentration of such centers and the density of electrons at these centers; \( \delta(x, y) \) represents the tunneling of electrons from a point defect to a dislocation or back again and is within the precision required—is of the form \( \exp[-(x^2 + y^2)^{1/2}/\hbar \omega_{st}] \); since in high-resistivity semiconductors only the deep strongly localized states are filled with electrons, it is found that \( \omega_{st} \) is of the order of the interatomic distance; \( P_{\text{in}} \) and \( P_{\text{out}} \) are the electron fluxes from a dislocation to the conduction band and from the valence band to a dislocation; \( P_{\text{in}} \) is the probability of release (per unit time) of an electron from an energy level \( E_D \) to the conduction band. The summation in Eq. (2) is carried out over the various types of impurity center.

The first term in the integrand in Eq. (2) describes the flux of electrons from a center \( E_D \) at a point \((x, y)\) to a dislocation; the second term represents the flux in the opposite direction. The flux of electrons from a unit length of a dislocation to the conduction band \( P_{\text{in}} \) was calculated by Shikin and Shikina\(^(1)\)

\[
P_{\text{in}} = \frac{1}{\hbar} \omega_{st} \exp \left( \frac{E_D - \mu}{kT} \right),
\]

where

\[
\begin{align*}
\omega_{st} &= \frac{2\pi e^2}{3\hbar} \left( \frac{\hbar}{kT} \right)^2 \exp \left( \frac{E_D - \mu}{kT} \right) \\
A &= \frac{2\pi e^2}{3\hbar} \left( \frac{\hbar}{kT} \right)^2 \exp \left( \frac{E_D - \mu}{kT} \right)
\end{align*}
\]

If

\[
E_D - \mu = 4(\ln((e^2/T) - 1) + \ln(T))
\]

FIG. 1. Schematic representation of the bending of the allowed energy bands near a dislocation and the coordinate system adopted in calculations.
The solution of the system of the steady-state equations $E$, satisfy the condition $d$ determines from the dislocation current $c_3'$, the conductivity semiconductors (only in such semiconductors can we determine $f$ from the dislocation current). The conductivity-electron density is very low ($<10^9$ cm$^{-3}$) even far from a dislocation, whereas near a dislocation the bending (rise) of the bands by an amount $-\Delta f$ allows the density to become complete negligible.

Subject to these comments, the system (2)-(3) becomes

$$
\sum_j \int \sigma(x, y) \{ e(x, y) (1-f) - \mu_e(x, y) \exp \left( \frac{E_0-E(x, y)}{kT} \right) \} dx
$$

$$
= \omega \left( \frac{\Delta f}{e} \right)^2 \exp \left[ \frac{E_0+\Delta f \ln(\mu_e/T) - 1}{kT} \right]
$$

(7)

$$
du(x, y) \mu_e(x, y) \{ e(x, y) (1-f) + \mu_e(x, y) \exp \left( \frac{E_0-E(x, y)}{kT} \right) \}
$$

(8)

where

$$
g(x, y) = \omega \exp \left[ \frac{(x+\Delta f)^2}{e} \right] \left[ 1 + \exp \left( \frac{E_0-E(x, y)}{kT} \right) \right]
$$

(9)

The solution of the system of the steady-state equations (7) and (8) is given in Appendix II:

$$
(1-f) = \omega \left( \frac{\Delta f}{e} \right)^2 \exp \left[ \frac{E_0+\Delta f \ln(\mu_e/T) - 1}{kT} \right]
$$

(10)

where the summation is carried out over all the levels $E_j$ satisfy the condition

$$
E_j = E_0 \ln \left( \frac{n_j}{n_j(0)} \right) \approx \Delta f = 0.6 \text{ eV}
$$

(11)

(for $f \approx 0.5$) and $R \approx 10^8$ cm.

We shall rewrite Eq. (10) in the form

$$
f = A \ln(\ln(\mu_e/T) - 1) - \frac{E_0 \Delta f}{kT} \sum_j n_j
$$

(12)

Since the expressions in the logarithm of Eq. (12) are much larger than unity, the main dependences of $f$ on $\mu$ and $T$ will be practically linear when plotted against $\ln \mu$ ($T \approx \text{const})$ and against $T$ ($\mu \approx \text{const})$. Therefore, in the experimental check on the theory, we shall concentrate our attention on the velocity and temperature dependences of $f$. Moreover, on increase in $n$ by several orders of magnitude (which occurs as a result of illumination with interband light), we may expect a considerable increase in $f$. Finally, in the experimental part, we shall compare the occupancy $f$, deduced from the equilibrium model in Read [Eq. (3)], with the value of $f$ deduced from Eq. (12) for parameters typical of ZnSe.

**METHOD**

We used $n$-type melt-grown ZnSe with the sphalerite structure and a room-temperature resistivity $\rho = 10^3 - 10^4 \Omega$ cm. Samples of $6 \times 4 \times 1.5$ mm were cut from ingots by a diamond saw and then ground with abrasive powders and polished with a diamond paste; next, they were subjected to chemical polishing in a solution of CrO$_3$ in HCl to remove the cold-worked layer. Indium contacts were deposited on the $6 \times 4$ mm face and the ohmic nature of these contacts was specially checked. The $1.5 \times 4$ mm face was parallel to the (011) plane and the (111) plane made an angle of $45^\circ$ with the long edge (6 mm) of the sample.

A sample was deformed by compression at a constant rate parallel to the long edge. The deformation rate was varied from 0.5 to 1000 $\mu$m/min. Selective etching in a mixture of $6$ g NaOH $+ 4$ g $K_2[Fe(CN)_{6}] + 50$ g $H_2O$ showed that plastic deformation was due to the motion of dislocations in a single plane (111), coinciding with the plane of stacking faults and making an angle of $45^\circ$ with the long edge of the sample. A study of the dislocations was at least two orders of magnitude higher than that of the $\beta$ locations, so that the measured charges were identical, to within $1\%$, with the charges of the $\alpha$ dislocations.

The dislocation charges were determined by the method of dislocation currents from the ratio of such a current to the rate of plastic deformation $\epsilon$. This method was described in detail elsewhere. $f = \phi/e$ We selected those ZnSe ingots for which, beginning from deformations of $2-3\%$, the value of $f$ was independent of the degree of deformation (up to $30\%$).

**EXPERIMENTAL RESULTS**

Figure 2 shows the dependences of the dislocation charge in ZnSe at various temperatures on the plastic deformation rate $\epsilon$. The dislocation charge is reduced to the electronic charge $e$ and multiplied by the distance between the broken bonds $b$, so that $\phi/b = \epsilon f$. The $\epsilon$ axis is logarithmic. In agreement with Eq. (10), we found that, in terms of these coordinates, $f$ was a linear function of $\ln \mu$ $\propto 20\%$ and the slopes of the lines increased with rising temperature. We deduced from Eq. (10) that...
We can see from Eq. (12) that the linear dependence of $f$ on $\phi h/\epsilon$ can be obtained from Eq. (12). The situation occurs if the $E_i$ centers lie below the Fermi level $\mu$ and the position of the latter is independent of temperature (for example, in the case of strongly compensated semiconductors such as the samples employed in our study). The $E_i$ centers lying above $\mu$ can, in this case, be ignored because of the low electron density $n_i$. However, $\mu$, because of the condition (11), a dislocation collects electrons from centers with $E_i > \mu (\mu - E_i > T)$, where $n_i = \exp ((\mu - E_i)/T)$, it then follows from Eq. (12) that $f(T) = \text{const}$, i.e., such centers can only give rise to a very weak (logarithmic) temperature dependence of $f$.

Finally, Fig. 4 shows the dependence $f$ on the wavelength $\lambda$ of light incident on a sample. It is clear from this figure that the illumination of ZnSe crystals increases $f$, as it does in the case of ZnS. The maximum of the spectral dependence occurs at the fundamental absorption edge. Under these conditions, the maximum number of electron–hole pairs is created in the bulk of a sample. The resultant electrons are captured by the empty trapping levels [the value of $2\mu R_{\text{dis}}$ in Eq. (12) increases]. It is less easy to explain why $f$ is affected by light of long wavelengths [the value of $2\mu R_{\text{dis}}$ in Eq. (12) increases] since the valence band–empty trapping level transitions should not occur beyond $h\nu = E_{\text{v}} - E_i > 2\text{ eV}$ ($\lambda < 6200$ Å). The only optical transition which can increase $f$ in this photon energy range seems to be the valence band–dislocation level transition. Therefore, we shall assume that the long-wavelength edge (1.5 eV) observed in the spectrum of Fig. 4 is associated with such transitions. Then,

$$E_{\text{v}} = -(E_i - 1.5 \text{ eV}) = -1.2 \text{ eV}. \quad (14)$$

Solving Eq. (10) for $E_{\text{v}}$ and assuming the parameters $\mu_i = E_i - h\nu \times 10^5 \text{ sec}^{-2}$, $\nu_i = 0.5 \times 10^5 \text{ cm/sec}$, $\mu_i - E_i - 10^5$ cm$^{-3}$ (deduced from the thermally stimulated conductivity and by the injected current method), $f = 0.5$, and $T = 0.025$ eV, we obtain $E_{\text{v}} = -1.3$ eV, which is very close to the value given by Eq. (14). In this estimate, the error in the value of $\mu_i R_{\text{dis}}$ amounting to two orders of magnitude can displace $E_{\text{v}}$ by just 0.1 eV.

We shall now estimate the occupancy of a dislocation at rest with an energy level $E_{\text{v}} = -1.2$ eV, which is in thermal equilibrium with the lattice. It follows from Eq. (1) that

$$f = \frac{1}{2\mu R_{\text{dis}}} \exp \left[\frac{\mu R_{\text{dis}}}{E_{\text{v}}} \cdot \frac{\mu R_{\text{dis}}}{E_{\text{dis}}} \right]. \quad (15)$$

If we assume that the screening radius $R_{\text{dis}}$ is governed by the concentration of the $E_i$ centers, i.e., $R_{\text{dis}} = (f/\mu R_{\text{dis}})^{1/3}$, we find that $f = 0.15$ at room temperature. If $R_{\text{dis}}$ is taken to be the Debye radius or the distance between the dislocations, the value of $f$ is found to be even smaller. Thus, a moving dislocation is characterized by a much higher electron occupancy than a dislocation at rest.

APPENDIX I

Equations (7) and (8) describe the variation of the electron density at impurities $n(x, y)$ with time or space. In view of the assumed homogeneous distribution of the impurity centers in space ($\delta r = \text{const}$), the function $n(x, y)$ should be stationary in a coordinate system linked to the core of a moving dislocation (Fig. 1). The system (7)–(8) is easier to solve because transitions between the smooth parts of the distribution function occur at distances between an impurity center and a dislocation which are, on the one hand, much greater than the lattice constant and, on the other, such smaller than the screening radius $R_{\text{dis}} = 10^4$ cm. Therefore, the electrostatic potential acting on an impurity because of the presence of a dislocation can be described by

$$\varphi = \frac{2\mu R_{\text{dis}}}{\mu R_{\text{dis}}} \exp \left[\frac{\mu R_{\text{dis}}}{E_{\text{v}}} \cdot \frac{\mu R_{\text{dis}}}{E_{\text{dis}}} \right]. \quad (1.1)$$

The solution of Eq. (8) for an impurity center $E_i$ is then

![Graph showing temperature dependence of $f$](image-url)
However, at these distances, the probability of electron transfer from a dislocation, \( R, \), to an impurity is exponentially small, \( \exp(-R, /a) \). Consequently, the impurity centers move away from a dislocation in the empty state. The reverse is true for \( R, < R, \). In the opposite case of \( R, > R, \), the probability of electron loss from a dislocation to an empty level \( E, \) becomes greater, beginning from distances \( R, \), and the level \( E, \) is filled right up to distances \( R, \) because the loss of an electron from a dislocation to the corresponding center is preferred to the opposite process.

At distances shorter than \( R, \), the density of the electrons at the \( E, \) center is low. We shall now consider the situation at the tail end of a dislocation. If \( R, < R, \), the flux from a dislocation to an impurity exceeds the reverse flux, beginning only from distances greater than \( R, \). However, at these distances, the probability of electron transfer from a dislocation to an impurity is exponentially small, \( \exp(-R, /a) \). Consequently, the impurity centers move away from a dislocation in the empty state. The reverse is true for \( R, > R, \). Then, beginning from distances \( R, \), the impurity centers become filled with electrons from a dislocation and they move away from it in the filled state. A graphical solution of Eq. (1.3) is shown in Figs. 4a and 4b. It is worth noting another interesting detail of this solution: transition from one smooth part of the distribution to another occurs over distances of the order of the interatomic separation. In the case of \( R, < R, \), this is self-evident be-

\[
\phi(x) = \phi(x) \exp \left[ \frac{-R,}{a} \right]
\]


\[
(1.2)
\]

\[
\phi(x) = \phi(x) \exp \left[ \frac{-R,}{a} \right]
\]


\[
\exp \left[ \frac{-R,}{a} \right]
\]


\[
(1.3)
\]


\[
\exp \left[ \frac{-R,}{a} \right]
\]


\[
(1.4)
\]


\[
(1.5)
\]


\[
(1.6)
\]


\[
(1.7)
\]


\[
(1.8)
\]


\[
(1.9)
\]


\[
(1.10)
\]
the shorter of the two distances \( R_1 \) or \( R_2 \). This has made it possible to assume that, before the interaction with a dislocation, these centers have the electron density \( n_1 \rightarrow n_2 \). We shall justify this assumption by estimating the probability of an electron transition from a level \( E_1 \) to the conduction band when the distance between the center with this level and a dislocation varies from \( R_1 \) to \( R_2 \). In such estimates, the important range of distances is that exceeding \( R_1 \), but smaller than a certain value \( R_c \). Beginning from \( R_c \), an electron from the level \( E_1 \) is transferred to the conduction band not at a given point in space but as a result of tunneling over a certain distance. An analysis similar to that used in calculations of the tunneling of an electron from a dislocation to the conduction band\(^{14}\) gives the following result:

\[
P(x,E_1E_2) = \pi \left[ \frac{A(x)}{T} \right] \exp \left[ \frac{A(x)}{T} \left( \frac{R_1}{x} - \frac{R_2}{x} \right) \right].
\]

where \( P(x,E_1E_2) \) is the probability of a transition (per unit time) of an electron from \( E_1 \) to the conduction band in the field of a dislocation at a point \( x \), \( E_2 \) is the same probability but outside the dislocation field, \( R_1 = \pi A(x)/T \), where \( r \) is the order of the interatomic distance. The quantity in the argument of the exponential function in Eq. (1.1) is of the order of \( (R_1 - x)/R_2 \) when the difference between \( x \) and \( R_1 \) is small. The values of \( R_1 \) and \( R_2 \) are of the same order of magnitude and, even if they differ by a factor of 3, we have

\[
\exp \left( \frac{A(x)}{T} \frac{R_1}{x} - \frac{R_2}{x} \right) = \exp \left( \frac{A(x)}{T} \frac{R_2}{x} - \frac{R_2}{x} \right).
\]

The probability of thermal release of an electron from a level in a time \( dt \) is:

\[
P_{\text{rel}} = \frac{c}{e} \exp \left( \frac{E_1 - E_2}{T} \right) dt.
\]

where \( c \) is the thermal velocity of the electrons, \( e \) is the electron-capture cross section of an \( E_1 \) center, \( N_e \) is the effective density of states in the conduction band, and \( g = 2 \). Without allowance for the tunneling in the dislocation field (at room temperature), we have

\[
P_{\text{rel}} = 10^{\frac{0.7 \times 10^{-10} - 10^{-10}}{2}} \exp \left( \frac{0.003}{10^{10}} - 10^{-10} \right) \times 10^{-4} \text{cm}^2/\text{sec}
\]

\[
\frac{R_2}{e} = \frac{R_2}{e} \times 10^{-4} \times 10^{-10} \text{cm}.
\]

The possibility of an indirect transition in the electric field of a dislocation at distances \( R_2 - R_1 \) contributes the following amount to this probability:

\[
dt \cdot P_{\text{rel}}(E_1E_2, \phi) = \frac{R_2 - R_1}{e} \times 10^{-4} \text{cm}.
\]

i.e., the probability of thermal release of an electron from filled levels \((E_2 < -0.7 \text{ eV})\) is negligible up to the moment when a given center is emptied because of the transfer of an electron to a dislocation. Therefore, we may assume that, up to distances of the order of \( 10^{-6} \text{ cm} \), we have \( n_1(x) = n_2(x) \).

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