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and M. Kaminska

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**PERSISTENT PHOTOCONDUCTIVITY DUE TO
NEGATIVE U CENTERS IN COMPOUND
SEMICONDUCTORS**

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ABSTRACT

It is shown that dopants in semiconductors exhibiting low temperature persistent photoconductivity should always have a paired electron ground state (negative U) if the electronegativity of the dopant is similar to that of the host lattice atom it substitutes. Half of the dopant atoms in the ground state should be in the single positive charge state and the other half in the single negative charge state. Negative U pairing is predicted specifically for the DX centers in AlGaAs.

The DX centers are deep donors formed when $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for $0.23 < x < 0.60$ is doped with a group IV or a group VI impurity. These donors show a number of unusual properties.^{1,2} First, the electron capture is thermally activated with a large capture barrier, which results in persistent photoconductivity at low temperatures. Secondly, DX centers exhibit a huge Stokes shift. Their optical ionization energy is about 1eV, whereas the thermal Hall activation energy is ten times less, about 0.1eV. The same properties were observed in other donor doped semiconductors such as chalcogen-doped GaAsP³, GaSb:S⁴ and CdTe:Cl⁵. Similarly, in CdF₂:In the deep, relaxed state with a thermal ionization energy of 0.2eV and an optical ionization energy of 1.9eV can be persistently converted by light into a shallower, hydrogenic state. In this state both, the thermal and the optical ionization energies are 0.1eV.⁶⁻⁸

Lang et al.^{1,2} suggested that the observed huge Stokes shift indicates a defect undergoing large lattice relaxation. This was considered to only be consistent with the defect being a complex. He proposed that the DX centers consist of a substitutional donor ("D") in a complex with an unknown intrinsic defect ("X") like a vacancy.

Recently the DX-like behavior was also observed when n-type GaAs was subjected to hydrostatic pressure.^{9,10} This finding allowed to conclude that the DX-center is in fact an isolated donor atom which depending on the band structure can undergo lattice relaxation.⁹ In addition it was recently shown that the far infrared optical absorption of the DX centers in AlGaAs in the metastable state is typical for 1s - 2p transitions of a hydrogenic donor.¹¹

Morgan suggested to explain the properties of the DX center by a donor atom undergoing a Jahn-Teller type distortion.¹² According to his model, the degenerate unoccupied hydrogenic state associated with the L valley (which is higher than G in the direct bandgap region) undergoes a Jahn-Teller transition. As result of the Jahn-Teller distortion, this level ends up below the hydrogenic G-like level, so that occupation of this distorted state by an electron should result in energy gain. This Jahn-Teller model can explain many properties of the DX centers in a satisfactory way. However, this model is unable to explain why there is still persistent photoconductivity in the indirect bandgap region, for Al mole fractions above 0.43. In this case, the degenerate L-like or X-like hydrogenic levels are lower in energy than the G-like level. In this case we would have a classical Jahn-Teller situation when electron capture and lattice distortion should occur **without any barrier**. Thus the Jahn-Teller model implies the absence of the capture barrier in the indirect bandgap region and therefore is inconsistent with the persistent photoconductivity still observed in this case.

Toyozawa proposed the metastable behavior of the DX center to be caused by extrinsic self-trapping similar to that in a polaron.¹³⁻¹⁵ In the case of a polaron only the lattice distortion itself is sufficient to create a self-trapped state. In the case of the DX center lattice distortion alone is not sufficient (otherwise polarons would have been observed in undoped AlGaAs), but needs to be assisted by the donor impurity potential. On the other side, the short range donor

impurity potential alone is not sufficient to lead to electron localization, as otherwise the hydrogenic state would not exist even as a metastable state and no persistent photoconductivity would be observed. Only the sum of the attractive donor impurity potential and the negative lattice relaxation energy is enough to localize the electron. This phenomenon is called extrinsic self-trapping.¹³⁻¹⁷ Toyozawa showed that the electron is expected to be localized completely, within the radius equal to interatomic bond length, within the dopant - centered first coordination tetrahedron.

It is worth to consider how this localization should occur in a multivalley semiconductor like AlGaAs. The kinetic energy of localization within the impurity centered first coordination tetrahedron is $p^2/2m^* \sim \hbar^2/(2m^*a^2)$, where p is the electron momentum, m^* the effective mass, and a the interatomic distance. If this energy is much larger than the lattice relaxation energy, formation of a deep donor state does not take place. This expression shows that extrinsic self-trapping can only happen if the effective mass is large enough. In the example of AlGaAs it explains why electron capture does not occur through the Γ valley with the small effective mass, but rather through L or X valleys¹⁸ ($m^*_{\Gamma}(\text{GaAs}) = 0.067m_0$, $m^*_L(\text{GaAs}) = 0.22m_0$, $m^*_X(\text{GaAs}) = 0.60$ ¹⁹). The use of the L or X-valley effective mass to describe the kinetic energy of an electron at the DX center is justified to the extent that the DX level follows the L or X valley and therefore the wavefunction of the DX state is built up from the wavefunctions of the electrons at the bottom of this valley.²⁰

This extrinsic self-trapping model seems to consistently describe all experimental data of different donor doped semiconductors, exhibiting persistent photoconductivity,¹⁻⁵ and of $\text{CdF}_2:\text{In}$ ⁶⁻⁸ where the lattice relaxation inducing phonon mode is shown by Raman experiments to be fully symmetric.²¹

In the following, the extrinsic self-trapping model resulting in formation of a deep donor state will be extended further by comparing the energy gained by trapping of a single electron with that of an electron pair. The lattice relaxation energy for a single trapped electron is $-V^2/2M\omega^2$ where V is electron-phonon interaction constant and $M\omega^2$ is the force constant of the trapping phonon mode. If an electron pair rather than a single electron is trapped, $2V$ should be substituted for V in this expression and the lattice relaxation energy **quadruples**. The lattice relaxation energy **per trapped electron** therefore **doubles** if all electrons are paired up (no electrons at half of the donors, two electrons at the other half of the donors). If the gain in lattice relaxation energy offsets the energy of interelectronic repulsion of electrons paired up at the same site, i.e. if

$$V^2/(2M\omega^2) > 1/2[e^2/(e_0 r_{el-el})] \quad (1)$$

then the electrons would pair up spontaneously, giving rise to a negative U system (Anderson's criterion²²). There are several known examples of negative U defects due to

lattice relaxation, such as interstitial boron and the vacancy in silicon²³⁻²⁵ and the M-center in InP.²⁶⁻²⁸

A simple consideration of the lattice relaxation energy shows, that the configuration dependent part of the energy density

$$\begin{aligned} E(Q) &= -VQ(r)n(r) + M\omega^2Q(r)^2 \\ &= M\omega^2[Q(r) - Vn(r)/(M\omega^2)]^2/2 - n^2(r)V^2/(2M\omega^2) \end{aligned} \quad (2a)$$

where $Q(r)$ is the distortion field, $n(r)$ is the electron density at the point r . The minimum of (2a) is achieved at

$$Q(r) = Vn(r)/(M\omega^2) \quad (2b)$$

and is equal to

$$E_{\min}(Q(r),r) = -n^2(r)V^2/(2M\omega^2). \quad (3)$$

Since the electron density $n(r)$ is inversely proportional to the localization volume of the electron, the minimized configuration dependent energy density (3) is therefore proportional to the inverse square of the localization volume. Integration of (3) over the localization volume gives that the **lattice relaxation energy is inversely proportional to the localization volume of the donor electron density**. This result, which follows from the simple equations (1) and (2), was also obtained by Toyozawa who used the variational method^{14,15}. Therefore the negative lattice relaxation energy increases with decreasing localization volume. In other words, the lattice relaxation energy tends to localize the electron as much as possible. However, the electron localization is limited by the length of the bonds to the first coordination neighbours. The only way to localize the electron density even further is to pair up electrons. Then the total localization volume of the electron density in the semiconductor would decrease by a factor of two and consequently the negative lattice relaxation energy contribution would increase by a factor of two. Thus, extrinsic self-trapping and negative U pairing are two subsequent steps to maximize the value of the lattice relaxation energy.

The first step, extrinsic self-trapping, can only occur if the sum of the resulting gain in lattice relaxation energy and the short term impurity potential offsets the increase in kinetic energy. The second step, negative U pairing, will occur if the resulting gain in lattice relaxation offsets the increase in coulombic repulsion energy of the two self-trapped electrons. Below we shall show that the kinetic energy in the localized state is greater than the interelectronic coulombic repulsion energy by a factor of $r_b/a \gg 1$, where r_b is the Bohr radius of the hydrogenic state. Thus, in most cases the criterion for extrinsic self-trapping is more restrictive than the criterion for negative U pairing. Therefore negative U pairing should be expected in the systems exhibiting persistent photoconductivity at low temperature. An example of experimentally proved concomitant persistent photoconductivity and negative U is the M-center in InP.²⁶⁻²⁸ Only if the electronegativity of the donor atom is much greater than that of the lattice atom it

substitutes, so that the electron energy in the short range potential of the donor is greater than the lattice relaxation energy, no negative U pairing can be expected.

Toyozawa's criterion for extrinsic self-trapping of a single electron on the donor atom is¹³⁻¹⁶:

$$-e^2/(e^*a) - e^2/(e_0a) - W - V^2/(2Mw^2) + Ch^2/(2m^*a^2) < 0 \quad (4)$$

where the left hand side of inequality (4) is the total energy. The expression $e/(e^*a)$ in the first term is the depth of the potential well created by polarization of the ionic solid, i.e. by displacement of cations towards the electron and displacement of anions away from the electron with $1/e^* = 1/e_0 - 1/e_{opt}$, where e_0 and e_{opt} are static and optical frequency dielectric constants, respectively. The second term is the electron-nucleus coulombic attraction energy. W is the short-range part of the impurity atom potential, determined by the chemical properties of the impurity, in particular by its electronegativity. $V^2/(2Mw^2)$ is the lattice relaxation energy. $Ch^2/(2m^*a^2)$ is the kinetic energy of electron localization, C is a constant of the order of unity.

If the radius of the hydrogenic state is much greater than the lattice constant: $r_b \gg a$, then all the Coulombic terms in (4), the first and second terms, can be neglected. Indeed, identity transformation of the ratio of coulombic energy to the localization energy yields

$$\begin{aligned} e^2/(e_0a) / [h^2/(2m^*a^2)] &= [e^2/(e_0r_b) / (h^2/(2m^*r_b^2))] a/r_b \\ &= 2a/r_b \\ &\ll 1, \end{aligned} \quad (5)$$

since $e^2/e_0r_b / [h^2/(2m^*r_b^2)] = 2$ (the ratio of potential to kinetic energy of the electron in the hydrogenic state is always equal to -2). Neglecting Coulombic terms in (5) we obtain

$$W + V^2/(2Mw^2) > Ch^2/(2m^*a^2) \quad (6a)$$

At the same time, the short range impurity potential W by itself should be less than the kinetic energy, because otherwise the electron would always be localized even without lattice relaxation and the hydrogenic state wouldn't exist even as a metastable state, i.e. we have

$$W < Ch^2/(2m^*a^2) \quad (6b)$$

Up to this point, no assumptions were made. For an estimate of the relative orders of magnitude of the short range impurity potential W and the lattice relaxation energy, one should notice that **any** group IV or group VI donor in AlGaAs forms the DX center, regardless of its chemical properties and with consequently different W values. For inequalities (6a) and (6b) to be fulfilled for all donors with different W values, the short range potential W should be of the same order of magnitude or less than the lattice relaxation energy. Then W should play a secondary role in (6a). One may therefore conclude that the lattice relaxation energy $V^2/(2Mw^2)$ is at least of the same order of magnitude as the kinetic localization energy

$Ch^2/(2m^*a^2)$:

$$V^2/(2Mw^2) \sim Ch^2/(2m^*a^2) \quad (7)$$

Here it was taken into consideration that r_{el-el} in the completely localized state is of the order of interatomic distance a and the electron-electron repulsion energy and thus the electron-nucleus attraction energy are of the same order of magnitude

$$e^2/\epsilon_0 \langle 1/r_{el-el} \rangle \sim e^2/\epsilon_0 a \quad (8)$$

Using (8) in (5) and substituting the result in (6), we come up with Andersen's negative U criterion (1). This means: **all defects with weak short range potential (of the chemical origin) that show low temperature persistent photoconductivity are expected to be negative U centers.** In the limiting case of infinite Bohr radius ($r_B/a \rightarrow \infty$) of the metastable hydrogenic state, all the dopants that show low temperature persistent photoconductivity should be negative U, regardless of the value of the short range impurity potential W .

The negative U property of the DX center implies that the neutral charge state of it is unstable against the disproportionation reaction:



In some cases, the neutral, but distorted DX^0 state may not even exist as an excited, unstable state, as the lattice relaxation energy due to capture of one electron may not be enough to offset the kinetic energy increase due to electron localization. If two electrons instead of one are captured, the lattice relaxation energy quadruples and consequently the lattice relaxation energy per captured electron doubles. Therefore the situation may occur when the lattice relaxation energy due to capture of an electron pair is enough to lead to localization of the electron pair, whereas at the same time the lattice relaxation energy due to capture of one electron is not enough to lead to localization of this electron (see configuration coordinate diagram on Fig.1). At the same time the metastable, undistorted state of the DX center is still a hydrogenic state with only one electron.

The conclusion about negative U properties of the DX centers in AlGaAs as well as most of the other deep donors which give rise to persistent photoconductivity enables us to explain some experimental data, otherwise inexplicable.

(1) No electron paramagnetic resonance (EPR) signal from the DX center, nor from In donors in bulk $CdF_2:In$, have been reported²⁹. An own detailed EPR study was performed on MBE grown 10mm thick $Al_{0.36}Ga_{0.64}As$ doped with $10^{17}/cm^3$ Si. Five samples were sandwiched together for increased sensitivity. However, we did not observe any EPR signal from the DX

centers. This result is difficult to understand if Si donors are assumed to be in the neutral, paramagnetic state. In that case the total number of spins would be well above the sensitivity limit of the EPR spectrometer. This negative result is indicative for the singlet pair formation due to negative U coupling of electrons, so that diamagnetic Si^- and Si^+ species are formed.

(2) Hall mobility often increases during photoionization of the DX center^{19,30,31}. This is just the opposite of what we would expect if all Si donors before photoionization were in the neutral charge state. In this case there would be no charged impurity scattering before illumination, giving a high Hall mobility value. After illumination, most donors should be in the D^+ charge state and the ionized impurity scattering would result in a low Hall mobility, much lower than before illumination. This is just the contrary to what is observed. The increase in Hall mobility after illumination is however understandable if half of the donors before illumination are assumed to be in D^+ charge state and the other half in the negative-U D^- charge state as predicted by the negative U model. In this case, the total number of charged scattering centers are not affected by photoionization, which converts negative-U D^- ions into D^+ ions. Since a negatively charged ion scatters just as efficiently as a positively charged ion, the mobility is not expected to change in the first approximation. Some increase in mobility after illumination may be explained by Debye screening of coulombic potential of the ionized impurity by the conduction electrons formed upon photoionization.

Further own experiments to directly prove negative U properties of the DX center are in progress.

In conclusion, we propose that a dopant impurity in a semiconductor which gives rise to persistent photoconductivity should be a negative U center if its electronegativity is similar to that of host lattice atom it substitutes. This applies specifically to the so-called DX-centers in AlGaAs.

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FIGURE CAPTION

Figure 1: Proposed configuration coordinate diagramm for the DX center. The thin line shows the energy of the donor without electrons, the dashed line with one captured electron, the thick line with two captured electrons. Q_0 , Q_2 are distortions corresponding to 0 and 2 captured electrons, respectively.

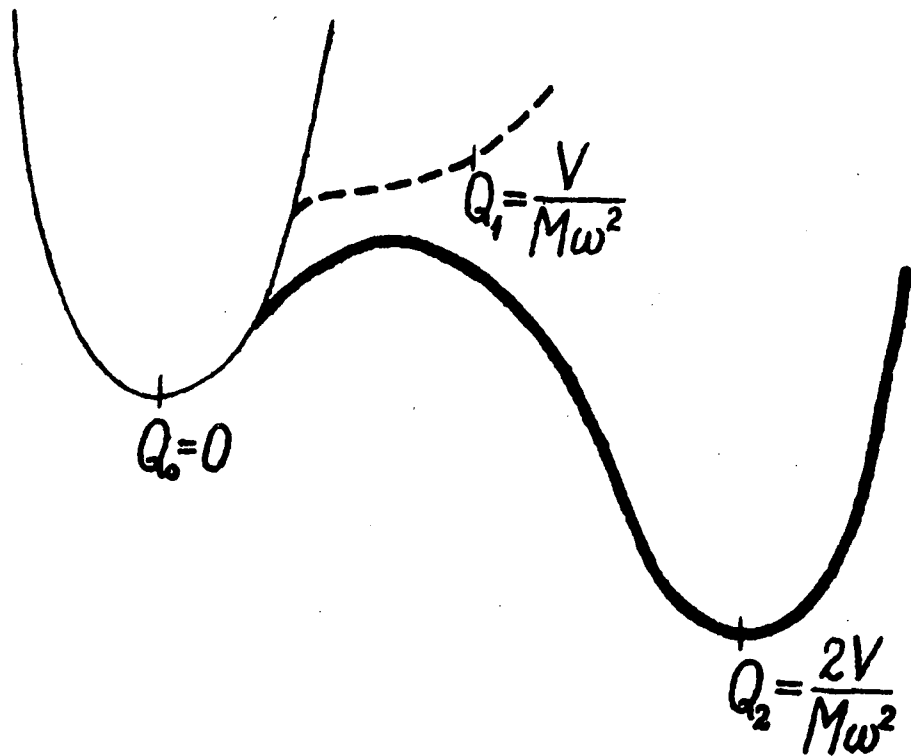


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