Spontaneous Tunnel Transitions Induced by Redistribution of Trapped Electrons over Impurity Centers

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Z. Naturforsch. **38a**, 959–962 (1983); received November 9, 1982

A system of polyvalent impurity centers in a semiconductor (i.e. Au-centers in Si) is considered. The ground state of the impurity pair Au^- (a) + Au° (b), where an extra electron is localized on the site a, may be turned into an excited state due to a change of the charge state of a third nearby impurity site. This happens because of different shifts of the Au^--level at sites a and b due to their different distances from the third center. As a result, the original pair is able to reach a new ground state Au° (a) + Au^- (b) through a slow spontaneous tunnel transition. The probability of this transition, when it is accompanied by an emission of a low energy photon, is calculated explicitly.

1. Introduction

Consider a semiconductor with randomly located impurity centers which are able to accomodate various numbers of electrons. As two examples of such impurities, we will mention here gold centers in silicon which can appear in various charged forms including Au^+, Au° and Au^--states and In-centers in PbTe [1, 2, 3]. The latter center may appear in three charge states: In^+, In^{2+}, and In^{3+}, which correspond to a negatively charged (In^+), neutral (In^{2+}) and positively charged (In^{3+}) state relative to the Pb^{2+} sublatice [1]. For the In: PbTe system the dissociation of a neutral impurity pair into positively and negatively charged impurity states (the process $2\,In^{2+} \rightarrow In^{3+} + In^+$) was shown to be energetically possible as a spontaneous reaction caused by polarization effects in charged states [1, 4].

Here we will discuss the possibility of another spontaneous tunnel effect, which has some physical similarity with the spontaneous dissociation considered in [1, 4]. It will involve, however, an interaction of a pair of polyvalent impurity centers with a third charged center. For concreteness, the discussion which follows uses Au-centers in Si as the most well known example of amphoteric impurities, although this does not restrict the general character of our consideration.

2. Radiative tunnel transitions in three-center complexes

Let us consider a pair consisting of negatively charged and neutral impurities (e.g. Au^- and Au° in Si) located at lattice sites a and b, respectively, separated by the distance R_0. If there are no other impurities in the crystal, then the one-electron states (I) Au^- (a) + Au° (b) and (II) Au° (a) + Au^- (b) are strictly degenerate and (provided we disregard the possibility of the effect described in [1, 4]) the true ground state of the system is a symmetrical combination of these states (i.e. the extra electron is equally shared between the sites a and b). Note that this spontaneous symmetrization of an electron between two equivalent sites can also be envisioned as the formation of a state similar to a molecular orbital.

Now let us assume that there is a third charged defect somewhere in the vicinity of this pair at site c as shown in Figure 1. To be specific, let us take this third center to be a singly positive charged center. It can be any positively charged impurity center, not necessarily an Au^+-ion. For simplicity, we place the site c on the same line as the Au^- (a) and Au° (b)-centers and closer to the site b, at a distance R_1 from the site b. For convenience, let us denote this system as (Au^-, Au°, pos)-system, where “pos” stays for a positively charged center and the order of symbols in parenthesis corresponds to their geometrical position in a linear array.

If the third center has a single positive charge, then the (vacant) energy level of the Au (b)-center

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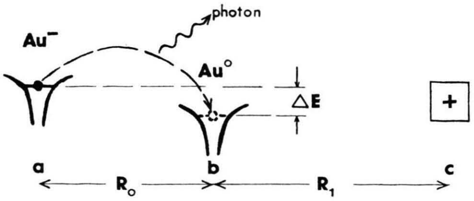

Fig. 1. The genesis of radiation unstability for an impurity pair due to the presence of a third charged defect (the case of (Au^-, Au°, pos)-linear array).

will be shifted downward relative to the same (occupied) level of the Au (a)-center by the amount of energy

$$\Delta E \cong \frac{e^2}{\varkappa R_1} - \frac{e^2}{\varkappa (R_1 + R_0)} . \quad (1)$$

Here $\varkappa$ is the dielectric constant of the material; $R_1 \equiv |\boldsymbol{R}_c - \boldsymbol{R}_b|$ and $R_0 \equiv |\boldsymbol{R}_a - \boldsymbol{R}_b|$, where $\boldsymbol{R}_a$, $\boldsymbol{R}_b$, and $\boldsymbol{R}_c$ are the radius-vectors of sites a, b, and c respectively.

The states I and II of the defect pair are no more degenerate and a possibility of the actual sharing of an extra electron between both sites is now determined by a competition between the resonance (energy transfer) integral V and the energy difference ΔE. if $V \ll \Delta E$, then the initial state Au^- (a) of an extra electron on site a is localized in the sense of Andersen localization (see, e.g. [5]). No electron symmetrization between sites a and b occurs and the pair states I and II are two distinct states separated energetically by the gap ΔE. Consequently, it is energetically possible (with an energy gain ΔE) for an outer electron of the Au (a)-center to go spontaneously on the vacant trapping level of the Au (b)-center.

The process

$$Au^- \,(a) + Au^\circ \,(b) \rightarrow Au^\circ \,(a) + Au^- \,(b) \quad (2)$$

may occur as a spontaneous radiative tunnel transition (RTT) with the emission of a low energy photon with energy ΔE [6, 7] or with the emission of a phonon(s).

Here we will calculate explicitly the probability of the RTT given by (2). This gives a *lower* estimate for the total tunneling rate because we are considering *only* the radiative contribution and ignore the probability of a phonon process. We also assume that the temperature of the crystal is low and therefore the possibility of thermal excitation and phonon assisted electron jumps can be disregarded.

The wave functions of the initial (before RTT) and final (after RTT) states of the outer electron of the Au^--center can be represented in the following form:

$$\begin{aligned} \psi_i(\boldsymbol{r}) &= \varphi(\boldsymbol{r} - \boldsymbol{R}_a) , \\ \psi_f(\boldsymbol{r}) &= N_f \{\varphi(\boldsymbol{r} - \boldsymbol{R}_b) + A\, \psi_i(\boldsymbol{r})\} , \\ \varphi(\boldsymbol{r}) &= \sqrt{\frac{\gamma}{2\pi}} \cdot \frac{e^{-\gamma r}}{r} . \end{aligned} \quad (3)$$

Here $\boldsymbol{r}$ is the radius-vector of the outer electron and $A\, \psi_i$ is the orthogonalization factor.

We used a delta well approximation for the orbital $\varphi(\boldsymbol{r})$ of the extra electron of the Au^--center; a similar approach was used earlier in our treatment of the RTT contribution to the strong electric field hopping conductivity in semiconductors [8, 9].

From the condition of orthogonality $\langle \psi_i | \psi_f \rangle = 0$ one can obtain

$$\begin{aligned} A &= -\langle \varphi(\boldsymbol{r} - \boldsymbol{R}_b) \,|\, \varphi(\boldsymbol{r} - \boldsymbol{R}_a) \rangle \\ &= -\exp(-\gamma R_0) . \end{aligned} \quad (4)$$

For the time constant of the RTT process we use the known equation for the spontaneous radiative decay [8, 9]

$$\frac{1}{\tau_{RTT}} = \frac{4}{3} \alpha^3 (\Delta E)^3 |\langle \psi_i(\boldsymbol{r}) \,|\, \boldsymbol{r} \,|\, \psi_f(\boldsymbol{r}) \rangle|^2 . \quad (5)$$

where $\alpha = e^2/\hbar c = 1/137$ is the fine structure constant and ΔE is the effective transition energy given by (1).

Note, that the orthogonalization procedure is necessary in order to avoid indefiniteness in the calculation of the coordinate matrix element in (5) due to various possible choices of the origin of the $\boldsymbol{r}$-vector. Note also that we are using here the same value γ for the fall off constant of the wave function of the Au^--outer electron in both the final and initial states, i.e. we ignore a small contraction of the outer electron cloud caused by the slightly lower (by the value of ΔE) energy position of the b-site relative to the a-site.

Bearing in mind that the normalization factor N_f is approximately unity and substituting (3) and (4) into (5) we obtain

$$\frac{1}{\tau_{RTT}} = \frac{\alpha^3}{3} (\Delta E)^3 R_0^2 \exp(-2\gamma R_0) . \quad (6)$$

Table 1. Transition energy and time constant for the radiative tunnel transition in the system $Au^- + Au^\circ +$ positively charged defect; the orbital of the outer electron of the Au^--center is $(\gamma/2\pi)^{1/2} \exp(-\gamma r)/r$ with $\gamma^{-1} = 10$ Å.

R_0 Å	R_1 Å	ΔE eV	τ_{RTT} s
50	50	0.01220	5.11
50	100	0.00407	138
100	100	0.00610	2.25×10^5
100	200	0.00203	6.07×10^6

For numerical calculations, let us take $\gamma^{-1} = 10$ Å, which is a realistic estimate for the decay constant of a rather loosely bound outer electron of the negatively charged Au^--center; for Si $\varkappa = 11.8$. The values of ΔE and τ_{RTT} calculated with (1) and (6) for a few combinations of R_0 and R_1 are given in Table 1.

From these results one can conclude that for many similar three-center impurity complexes the expected rate of RTT will be extremely low. The reason for this is the exponential decrease of the probability of RTT with tunneling distance.

3. Discussion

The very existence of the energetic possibility of spontaneous transitions of individual electrons onto lower lying empty levels means that the original state of the whole many-electron system is not a genuine ground state in a strict quantum mechanical sense. Thus, the whole consideration given here can be objected on the ground that for a crystalline system with a fixed impurity distribution all spontaneous transitions have been "already" occurred no matter how large the values of τ_{RTT} could be for some of these transitions.

This argumentation, however, silently supposes that the impurity system was prepared very long ago and consequently no changes are allowed to happen at the "present time". This is, of course, true for any system, provided it is in its genuine ground state. For many experimental situations this condition may appear, nevertheless, not to be the case. In practical terms, almost any observable ("as prepared") state of the impure crystal (even if temperature → 0) has a certain degree of excitation due to the existance of a whole variety of very slow tunneling processes. Our present estimate (see Table 1) shows that for typical impurity subsystems the radiative transition rate τ_{RTT} is very low. It seems to us unlikely that the explicit inclusion of tunneling transitions accompanied by the emission of phonon (their probability should also include the same small exponential factor as in (6)) could substantially enhance the total tunneling transition rate. The nonradiative mechanism can, however, be predominant for two-site tunneling recombination processes [10], when two different centers are involved and consequently ΔE has a non-zero value by itself and not as a result of an external perturbation.

A sudden elementary excitation (absorption of an external photon, fast particle, annihilation of an exciton, etc.) may lead to a redistribution of charges between two or more impurity centers. As a result, a certain number of electronically excited impurity subsystems can be created in the vicinity of the just recharged centers. In terms of the above example (Au^-, Au°, pos)-system (Fig. 1), the ionization of one impurity center and the subsequent trapping of the released electron by another center may result in the formation of one or a few impurity subsystems able to slow spontaneous RTT.

Suppose, for example, that due to random fluctuations of the crystalline potential the occupied level at site a (Au^--center) is slightly lower in energy than the corresponding empty level associated with the site b (Au°-center). Thus, the ab-impurity pair is in its ground state and no transitions with a release of energy are possible. Now suppose that an external photon ionizes the impurity center at site c converting it into a positively charged center whereas the released electron is removed and can be trapped by some distant defect.

The sudden appearance of a charged defect at site c may reverse the relative positions of the Au^--levels at sites a and b provided the geometrical and energy parameters of the (Au^-, Au°, pos)-subsystem are properly selected. This process, in fact, transforms the ground state of the pair Au^- (a) + Au° (b) into an excited state. This excited state has an exponentially small (although non-zero) dipole matrix element with the ground state; the last one now corresponds to the configuration Au° (a) + Au^- (b). This long-lived excited state can only conditionally be classified as a metastable state; the last term usually means a state from which the dipole transition to a ground state is strictly forbidden.

It is possible to indicate some other structures of long-lived defect subsystems of the same nature. For example, in an (Au°, Au^-, neg)-system, the filled level of the central Au^--ion can suddenly be raised if a nearby impurity happened to trap an extra electron. Provided the formation of the negative impurity site ("neg") reverses the relative position of the Au^--levels at both Au-sites, the configuration Au° (a) + Au^- (b) will be subjected to slow RTT to the ground state configuration Au^- (a) + Au° (b). To obtain the original "metastability", this raise of the filled Au^- level at site b (Fig. 1 with "+" replaced by "−" at site c) should exceed the sum of the smaller raise of the empty Au^--level and the original energy gap ΔE between the Au^--levels at sites a and b.

4. Concluding Remarks

We discussed here spontaneous tunnel transitions induced by the redistribution of trapped electrons over a system of impurity centers. As an elementary process, this kind of tunnel transition involves at least *three* impurity sites. Physically, the situation considered here means that the change of charge state of the third nearby impurity site turns the ground state of the original impurity pair into an excited state.

The possibility of the formation of a long-lived excited state of the two-center impurity complex arises from the sudden change of the local potential. This change happens as a result of trapping (or loss) of an electron onto (from) a nearby third impurity center.

Due to long-range character of the Coulomb interaction (illustrated here by (1)) the change of the charge state of a single impurity site may, in principle, generate not only one, but several reversed-level ("metastable") subsystems. These newly excited subsystems will slowly relax to their ground states through the RTT's intermixed with a certain amount of radiationless (phonon emitting) tunnel transitions. Aside from the mentioned essentially three-center character of the metastability discussed in the present paper, the RTT-relaxation process in itself is similar to the two-center RTT's considered in [6, 7, 8, 9]. The RTT-processes considered in these papers were substantially two-center processes. In the theory considered in [8, 9] the inversion of filled and empty energy levels is induced by the application of an external uniform strong electric field, rather than by microscopic fields of individual charged defects as in the present paper.

The long-lived RTT-able subsystems could include linear arrays like (Au^-, Au°, pos) or (Au°, Au^-, neg), their non-linear modifications, as well as more complex clusters. The breaking down of the total impurity system into such individual subsystems may be subject to a certain degree of arbitraryness.

The presence of the RTT's can appear in the form of weak long-lived infrared or microwave emission which would obviously not be easy to detect experimentally. In view of the slowness of RTT's and the great dispersion in the values of τ_{RTT} and ΔE for various subsystems, one should speak of the emission of individual random photons rather than of the radiation in the ordinary sense.

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