

# A new model for defects in chalcogenide, glass-like semiconductors

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(Submitted 18 February 1980)

*Pis'ma Zh. Eksp. Teor. Fiz.* **31**, No. 8, 437–440 (20 April 1980)

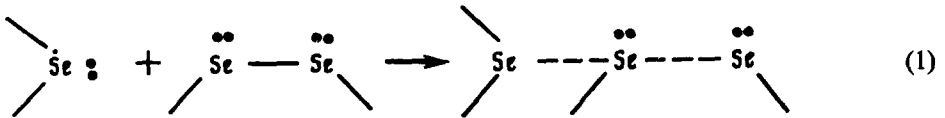
We propose a model according to which the neutral, diamagnetic quasi molecules, which are produced due to orbital-deficient bonds, must be the defects with the smallest production energy in the chalcogenide, glass-like semiconductors (CGS).

PACS numbers: 61.40.Df

A model, initially proposed in Refs. 1 and 2 and subsequently described in detail in Ref. 3, is widely used now to explain the peculiarities of the electronic properties of CGS. According to this model, the properties of CGS are determined largely by specific defects—atoms in unusual valence states. The state of a chalcogen atom in a glass is assumed to be normal when it forms two covalent bonds with its neighbors and, in addition, has an unshared pair of valence  $p$  electrons that do not participate in the binding. The symbol  $C_2^0$  was suggested for such state in Ref. 3, where the symbol  $C$  indicates that the atom belongs to the chalcogens, the superscript denotes the charge of the atom, and the subscript refers to the number of covalent bonds formed by it.  $C_1^0$ ,  $C_3^0$ ,  $C_1^-$ , and  $C_3^+$  were examined in Ref. 3 as the main defect centers in materials such as amorphous selenium. In order for the  $C_1^0$  centers to be produced, there must be a covalent bond breaking, which can be represented as the reaction  $2C_2^0 \rightarrow 2C_1^0$ . As a result of such reaction, the energy of the system must change by a rather large amount—equal to the energy of the covalent bond  $2\epsilon$ . As a result of conversion of the pair of  $C_2^0$  centers to the pair of  $C_3^0$  centers, the number of bonds in the system formally increases by unity. The energy of the system, nonetheless, increases by a certain amount  $2\Delta$  in this case, since the  $2C_2^0 \rightarrow 2C_3^0$  reaction is associated with the conversion of two pairs of unbound electrons (electrons of the unshared pairs of the two  $C_2^0$  centers) to a pair of bound electrons and a pair of bond-loosening (antibonding) electrons. Since  $\Delta$  is much smaller than  $\epsilon$ , the formation of the  $C_3^0$  center, as indicated in Ref. 3, requires a smaller energy than that for formation of the  $C_1^0$  center. In the  $2C_2^0 \rightarrow C_1^- + C_3^+$  reaction the number of covalent bonds in the system does not vary and the antibonding orbitals are not populated. However, the electron redistribution in the system, which leads to the appearance of charged centers, is attributable to a certain energy consumption  $U$ . This consumption is close in magnitude to the energy variation produced as a result of the  $2C_1^0 \rightarrow C_1^- + C_1^+$  reaction. Therefore, the value of  $U$  must be comparable with the ionization potential difference and with the electron affinity of the chalcogen atom, and this difference is very large ( $7-8$  eV). For this reason, the assertion in Refs. 3 and 4 concerning the validity of the inequality  $U < 2\Delta$ , which must be satisfied in order for the  $2C_3^0 \rightarrow C_1^- + C_3^+$  reaction to be exothermic, is unjustifiable. The only justification for this assertion was essentially based on the fact that, on the one hand, the  $C_2^0$  centers cannot be considered defects of lowest

energy, since they are paramagnetic, whereas the experiment indicates that the unpaired spins in the CGS are virtually missing under ordinary conditions, and on the other hand, the diamagnetic defects, whose formation energy would be smaller than that for the  $C_1^-$  and  $C_3^+$  pairs, cannot be constructed within the framework of this model.<sup>3</sup>

A more careful analysis of the valence possibilities of the chalcogen atoms shows, however, that only some types of defects, which can be present in the CGS, are examined in terms of the model of Ref. 3. Specifically, the CGS can have different quasi-molecular defects, which are produced due to formation of multicenter, orbital-deficient bonds analogous to those that provide stability of xenon fluorides or polyhalide molecules. For example, one of the simplest quasi-molecular defects in amorphous selenium can be produced as a result of the reaction



Here, the solid lines represent the ordinary covalent bonds, the dark circles denote the unshared pairs of valence  $p$  electrons, and the dashed line corresponds to the three-center, three-orbit, four-electron bond. The energy diagram of the reaction (1) is shown in Fig. 1.

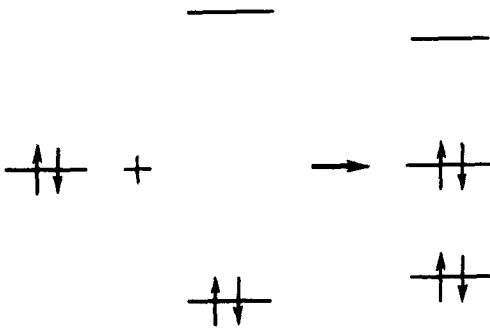


FIG. 1.

This diagram illustrates the important fact that in the examined reaction the number of electrons in the bonding and antibonding orbitals does not change as a result of substituting the three-center, orbital deficient bond for the two-center, covalent bond, the antibonding orbitals are not populated, and the  $C_1^-$ -type charged defects do not appear. We can expect, therefore, that production of this type of quasi-molecular defects should be energetically more advantageous than that of the defects examined in Ref. 3. It should also be noted that, within the framework of the model developed in Ref. 3, the neutral defects always turned out to be paramagnetic, and the diamagnetic defects turned out to be charged. The quasi molecule examined above is neutral and diamagnetic, i.e., it is an example of precisely this type of defects whose presence in CGS, as indicated in Ref. 4, is necessary for a consistent interpretation of the photoluminescence data. The production of quasi molecules also accounts for the photoinduced transformation in CGS. In particular, the reaction (1) can be initiated

by light irradiation with a frequency of the order of the width of the energy gap, since a transfer of one of the electrons of the unshared pair of a chalcogen atom in the normal valence state to the antibonding orbital of the covalent bond situated nearby is possible as a result of such irradiation. As a result, this bond is destabilized, and there can be a transfer of atoms such that it would give rise to favorable conditions for production of a quasi molecule. It is also important that the back reaction can proceed under thermal conditions, since it is related to that type of coordinated reactions which are resolved with respect to symmetry.<sup>5</sup> In this paper we limited ourselves to the example of 2 simplest quasi molecule. In fact, more complex quasi-molecular defects, including quasi complexes and polymer formations, can be produced in CGS. For a more comprehensive interpretation of the experimental data, they must be taken into account. In particular, the well-known effect of switching of the CGS from the state with a low conductivity to one with high conductivity can be explained by the production of polymer quasi molecules due to the influence of external electric field. In conclusion, we note that not only chalcogens but, for example, also elements of the fifth group of the periodic table can participate in the production of orbital-deficient bonds.

The author is grateful to S. A. Dembovskii and the participants of his seminar for a discussion of this work.

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<sup>5</sup>R. Woodward and R. Hoffmann, *Sokhraneniye orbital'noi semmetrii* (The Conservation of Orbital Symmetry), Mir, M., 1971. [Orig., Verlag Chemie, Weinheim, 1970.]