Model for bond-breaking mechanisms in amorphous arsenic chalcogenides leading to light-induced electron-spin resonance

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A model is presented for the light-induced bond-breaking processes in arsenic chalcogenides which, based on theoretical calculations of coordination defects, accounts for the details of recent experimental light-induced electron-spin resonance experiments on amorphous As_xS_{1-x} alloys. The presence of homopolar (wrong) bonds is essential in such compound materials for the optically induced creation of metastable paramagnetic dangling-bond defects, but the creation process does not involve the scission of such homopolar bonds themselves.

I. INTRODUCTION

Many studies of photoinduced defect creation in amorphous chalcogenides have been performed using light-induced electron-spin resonance (LESR) measurements;[1–5] of course, such measurements are only sensitive to the presence of *paramagnetic* defects. Two types of behavior may be distinguished. At low excitation intensities, the LESR signal saturates with time,[2] indicating that diamagnetic precursor (defect) states, already existing in the glass, are optically excited, forming paramagnetic centers after trapping of holes or electrons. On the other hand, at high excitation intensities, the LESR signal does *not* appear to saturate with time,[1,5] implying that the light-induced creation of paramagnetic defects is occurring. Furthermore, after thermal annealing of such irradiated glasses, reillumination causes at first a much faster inducing of the LESR signal, indicating that the initial illumination has created a set of metastable defects, which are in a diamagnetic state after annealing, and which can readily be photoexcited to produce paramagnetic states before further (bond-breaking) defect creation takes place.[1,5]

Recently, Hautala, Ohlsen, and Taylor[5] have shown that *four* different metastable LESR centers can be induced in a-As_xS_{1-x} by prolonged illumination. Two of the centers (labeled type I) are associated with a sulfur and arsenic atom, respectively, and are distinguished by annealing out at lower temperature (~ 180 K) than the other pair of defects (type II), also associated with sulfur and arsenic atoms, which anneal out at considerably higher temperatures (~ 300 K). There are further differences between the behavior of the type-I and type-II LESR defects. The concentration of the type-I defects (both S- and As-centered) is *independent* of the concentration in the alloy system As_xS_{1-x}, whereas As_{II} centers dominate in As-rich material, and S_{II} centers dominate for S-rich compositions. However, for the stoichiometric composition As_2S_3 ($x=0.4$), the As_{II} centers are approximately four times as numerous as the total As_I, S_I, and S_{II} concentration; the concentrations of As_{II} and S_{II} centers are only equal for the composition $x=0.37$.[4,5] Finally, although the ESR signatures of the S_I and S_{II} centers are very similar, and ascribed to a hole in a nonbonding sulfur p orbital (dangling bond),[2,5] the signatures of the As_I and As_{II} centers are appreciably different; the As_{II} centers have been ascribed to an almost purely p-like As dangling-bond orbital, whereas the As_I center appears to be rather more delocalized with a somewhat larger s-orbital contribution.[5]

There is also evidence for the photoinduced creation of *diamagnetic* defects in chalcogenide glasses in addition to that inferred from the LESR kinetics of reilluminated samples mentioned above.[1,5] We have recently reported[6,7] reversible photoinduced changes in the ac conductivity of a-As_2S_3 films (an increase in σ_{ac} after illumination, and removal of the change by annealing), which were interpreted in terms of the photocreation of self-trapped exciton (STE) states, viz., close pairs of oppositely charged (diamagnetic) dangling-bond defect states (e.g., P_4^+-C_1^-, where P is a pnictogen, C is a chalcogen, the superscript refers to the charge state, and the subscript refers to the coordination of the dangling-bond defect). In addition, changes in the photocurrent of amorphous chalcogenides under steady-state illumination are also interpreted in terms of the photocreation of charged (diamagnetic) dangling-bond defects, which act as trapping and recombination centers, and which therefore limit the photoconductivity.[8]

However, a detailed discussion of the mechanism of photocreation of both paramagnetic and diamagnetic defects, which is consistent with the available LESR evidence,[2,4,5] has not previously been given. Therefore, we give here a model for such photoinduced bond-breaking processes which is in accord with the available experimental evidence.

II. MODEL FOR PHOTOINDUCED DEFECT CREATION IN CHALCOGENIDE GLASSES

At the outset, it is important to emphasize three aspects, namely, the difference in defect behavior between

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compound chalcogenide glasses (e.g., As_2S_3) and elemental chalcogens (e.g., Se), the importance of homopolar or like-atom ("wrong") bonds, and the role played by π-bonding interactions. It is often thought that the dangling-bond defects that arise from the breaking of covalent bonds in chalcogenide glasses are normally neutral (e.g., P_2^0 or C_1^0) and hence paramagnetic, and that they give rise to defect states lying deep in the gap. However, these assumptions do not necessarily hold in the case of compound chalcogenide glasses, where the effects of ionicity (electronegativity differences) and the presence of homopolar bonds can exert a dramatic influence.

Vanderbilt and Joannopoulos have undertaken theoretical studies of various defect states in elemental systems[9,10] (i.e., Se) and in compound materials[11] (i.e., As_2Se_3), and their findings can be summarized as follows. In the case of *a*-Se, π interactions between the nonbonding (lone-pair) orbitals at a defect site and at a neighboring fully bonded chalcogen site give rise to bonding (π) and antibonding (π^*) combinations,[9] the latter of which gives rise to a deep-lying gap state and which is half-filled in the case of the $C_1^0(C)$ defect (where the symbol in the parentheses denotes the neighboring atom to the defect). However, in the case of compound chalcogenides, a similar defect connected to a fully bonded pnictogen does *not* experience such π interactions (since there are no As *p*-like nonbonding orbitals available), and as a result the defect only supports shallow acceptor levels and is negatively charged in its natural charge state [viz. $C_1^-(P)$]. Furthermore, it has been found[10] that, in the case of the pure elemental material (e.g., Se), the effective correlation (Hubbard) energy is *positive*, meaning that the neutral paramagnetic defect $C_1^0(C)$ is more stable than the charged diamagnetic configurations [$C_1^-(C)$, $C_3^+(3C)$].

In the case of pnictogen-based defects in compound chalcogenides, the type of nearest neighbors and the presence of π interactions also dictate the character and the position in the gap of the defect states.[11] Thus, for chemically ordered pnictogen-based dangling bonds [$P_2(2C)$], π interactions between the pnictogen *p*-like nonbonding orbital (NBO), p_P, and a neighboring *p*-like NBO on a chalcogen, p_C, give rise to a gap state $\pi^*(p_P - p_C)$, which lies in the upper half of the gap near the conduction band. Thus, if the Fermi level lies below this level, near midgap as usual, this As dangling-bond defect will be naturally positively charged [i.e., $P_2^+(2C)$]. However, if one or both of the neighboring chalcogen atoms is replaced by a pnictogen atom, thereby forming one or two *homopolar* bonds at the defect, such $P_2(P,C)$ or $P_2(2P)$ defects give rise to a purely *p*-like As NBO state lying close to midgap (and which would normally be half-filled making the defect neutral, i.e, P_2^0), with a lower (filled) state lying nearer the valence bond, arising from π interactions between the pnictogen-pnictogen *p*-like σ bonds adjacent to the defect and *p*-like NBO's on next-nearest-neighbor chalcogen sites [viz. $\pi^*(\sigma_P - p_C)$].

In summary, the theoretical calculations of Vanderbilt and Joannopoulos[9,11] indicate that in compound pnictogen-containing chalcogenide glasses (e.g., As_2S_3 and As_2Se_3), dangling bonds only give rise to localized deep gap states associated with neutral paramagnetic centers in the case when *homopolar* bonds are immediately adjacent to the defect [e.g., $C_1^0(C)$, $P_2^0(2P)$, and $P_2^0(P,C)$]. On the other hand, dangling-bond defects, at which the local bonding is chemically ordered [viz. $C_1(P)$

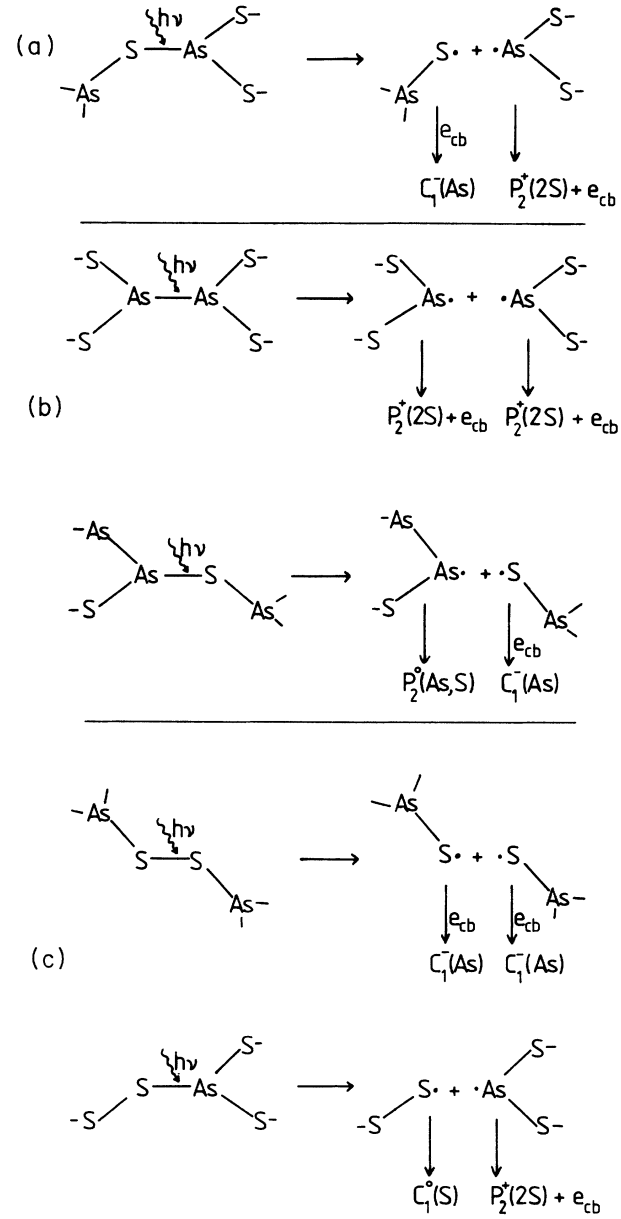

FIG. 1. Schematic illustration of the various types of optically induced bond-breaking mechanisms operative in amorphous arsenic chalcogenides in (a) a chemically ordered structure, (b) the vicinity of an As—As homopolar bond, and (c) the vicinity of a S—S homopolar bond. The resulting types of metastable dangling-bond defects are shown where the subscripts and superscripts to the symbols *P* (pnictogen) and *C* (chalcogen) refer, respectively, to the coordination number and charge states of the defects, with the type of nearest neighbors shown in the parentheses. Excess electrons, free to move in the conduction band, are denoted by e_{cb}.

and $P_2(2C)$], give rise to defect states which prefer to be charged and diamagnetic, i.e., C_1^- and P_2^+. The empty NBO associated with the P_2^+ center can, in principle, take part in further dative-bonding reactions with a nearby Se p-like NBO, thereby forming a C_3^+ center, or even with the s-like NBO of a nearby As atom, thereby resulting in an overcoordinated P_4^+ center at which sp^3 hybridization has occurred. These considerations will be of importance when considering the possible optically induced bond-breaking defect reactions to be discussed next.

In Fig. 1 we show the various photoinduced bond-breaking processes that can occur in a compound chalcogenide glass (e.g., As_2S_3) in the case of a chemically ordered structure [Fig. 1(a)], and when As—As and S—S homopolar bonds are present [Figs. 1(b) and 1(c), respectively]. The stable defect configurations resulting from such processes are also shown, taking into account the above discussion on defect energetics, but neglecting any further defect reactions which may take place involving P_2^+ or C_1^- centers in intermolecular ("interlayer") defect-transformation bond reconstructions.[12] The close pairs of defect configurations shown in Fig. 1 would be reasonably stable against annihilative reconstruction [except perhaps for the STE configuration P_2^+ and C_1^- shown in Fig. 1(a)] as long as the extra electrons liberated (into the conduction band) in the defect reactions (e_{cb}) were to migrate sufficiently far from the sites of the defects. Alternatively, the stability of the defects would be enhanced if they were to become more spatially separated as a result of the "interlayer" defect-conserving bond-flip reactions, such as those shown in Fig. 2. The facility of such interlayer reactions in compound chalcogenides has been illustrated recently by the theoretical calculations of Tarnow, Joannopoulos, and Payne,[13] which indicate that interlayer bonds can form readily in crystalline As_2Se_3, between two antistructure defects in adjacent layers but separated by a distance greater than the closest interlayer separations[14] (see Fig. 3).

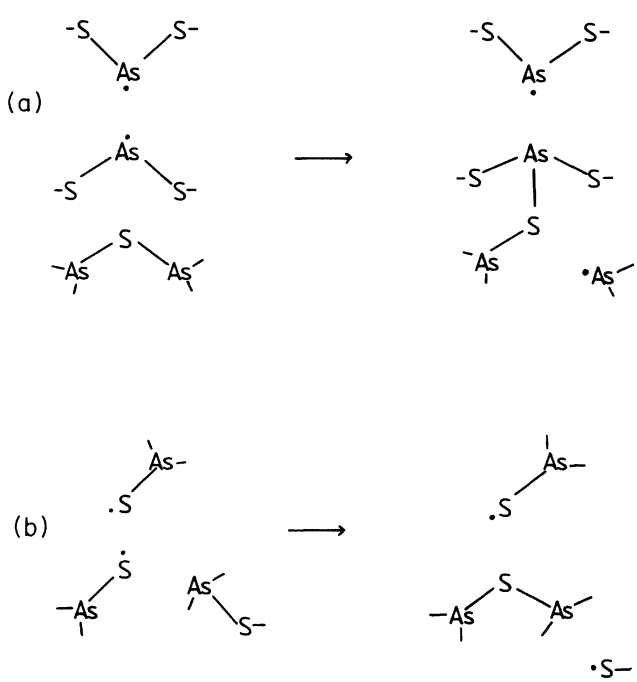

FIG. 2. Defect-conserving bond-switching mechanisms leading to an increased spatial separation of defects for (a) As dangling bonds and (b) S dangling bonds.

III. DISCUSSION

The defect creation reactions illustrated in Fig. 1 account for the recent LESR results observed in As_xS_{1-x} glasses.[5] We identify, for several reasons, the P_2^0(As,S) and C_1^0(S) centers, in Figs. 1(b) and 1(c), respectively, with the As_{II} and S_{II} defects found by Hautala, Ohlsen, and Taylor.[5] These P_2^0 and C_1^0 defects are expected to be reasonably stable in the light of the discussion given in Sec. II, and particularly so if the bond-flip reactions of the type illustrated in Fig. 2 separate them from their conjugate defect configurations. This would accord with the fact that the LESR signal, associated with type-II centers, anneals out only at the relatively high temperature of ~ 300 K;[5] this annealing process is ascribed to either the trapping or thermal excitation of a hole or an electron by or from the P_2^0 and C_1^0 centers, thereby transforming them into diamagnetic charged configurations (e.g., P_2^+ and C_1^-, etc.). (Dangling-bond defects in arsenic chalcogenide glasses are predicted theoretically to have negative effective correlation energies,[11] an assertion supported by the absence of dark ESR signals in such glasses.[2]) The ESR characteristics expected for the P_2^0(As,S) and S_1^0(S) defects also support their identification as the type-II LESR centers found in Ref. 5. Gaczi found that the ESR signal in S-rich As_xS_{1-x} glasses (dominated by S_{II} centers[5]) was best fitted by the ESR characteristics of the S_1^0(S) center, rather than by those of the S_1^0(As) defect.[4] In addition, fitting of the ESR line of the As_{II} center indicates that the unpaired spin associated with the defect has an almost 100% p-like character;[5] this behavior is expected[11] for the unpaired electron associated with the P_2^0(As,S) center [but not the P_2^0(2S) defect].

This identification of the type-II LESR centers in As_xS_{1-x}, and their creation mechanisms shown in Fig. 1(b) and 1(c), allows one to understand the previously puzzling finding of Ref. 5 that the As_{II} centers dominate, even for stoichiometric material ($x=0.4$). Examination of Fig. 1 shows that only the breaking of heteropolar (As—S) bonds *immediately adjacent* to a homopolar (As—As) bond leads to the $P_2^0(P,C)$ center identified here as the As_{II} defect. There is now considerable experimental evidence, for instance, from Raman scattering[15] and Mössbauer spectroscopy,[16] for the existence of a small concentration ($\sim 1\%$) of homopolar bonds, even in stoichiometric arsenic chalcogenide glasses; of course, the proportion of one type or the other of wrong bonds increases dramatically for off-stoichiometric compositions. Thus, for the stoichiometric composition As_2S_3, it is ex-

pected that there would be an equal number of As—As and S—S homopolar bonds (in a fully connected structure). Although heteropolar bonds are more stable thermodynamically than homopolar bonds in a compound material because of electronegativity considerations,[11,17] it may be assumed, to a zeroth approximation, that the quantum efficiency for optically induced bond breaking is approximately the same for all types of bond, both heteropolar and homopolar. With this assumption, the fact that there are four heteropolar As—S bonds immediately adjacent to each As—As homopolar bond, whereas there are only two such bonds immediately adjacent to each S—S homopolar bond, leads to the prediction that, for stoichiometric As_2S_3, twice as many As_{II} centers should be produced as S_{II} centers, with the total number of each being of the order of the number of wrong bonds in the glass, i.e., a fraction of $\sim 1\%$. Experimentally, the ratio of the number of As_{II} centers to S_{II} centers in *a*-As_2S_3 is somewhat larger,[5] i.e., $\sim$4:1, but the overall number of type-II LESR centers[5] ($\sim 10^{20}$ cm^{-3}) is indeed comparable with the expected proportion of homopolar bonds.[15,16] Note that the mechanism for the production of type-II LESR centers proposed here differs from that proposed by Hautala, Ohlsen, and Taylor,[5] who proposed that breaking of the *homopolar* bonds themselves was responsible.

We turn now to a discussion of the type-I LESR centers found in As_xS_{1-x} by Hautala, Ohlsen, and Taylor.[5] We identify these centers with electrons or holes trapped at P_2^+(2S) or C_1^-(As) centers, respectively (see Fig. 1).

The instability of the type-I LESR centers (annealing at $\sim$180 K) is ascribed here to the weak localization of the hole trapped in a hydrogenic acceptor level of the C_1^-(As) center in the case of S_I. In the case of As_I, it is assumed that the $\pi^*(p_{As}-p_{Se})$ levels of the P_2(2S) defects are sufficiently broadened by site-to-site disorder that they form into a band of states extending down through the gap and below E_F; in this case, those centers with levels lying near E_F would be singly occupied, and hence neutral and paramagnetic, but could easily be thermally transformed to the diamagnetic P_2^+ state.

The ESR signature of the C_1^0(As) center is expected to be rather similar to that of the C_1^0(S) center,[4] and experimentally it is found that the ESR line shapes of the S_I and S_{II} centers are very alike.[5] Nevertheless, detailed computer simulation of the ESR line shapes should, in principle, allow the two types of chalcogen-based paramagnetic centers to be distinguished, and thus the identification of the centers S_I^0 with C_1^0(As) and S_{II}^0 with C_1^0(As) to be directly tested experimentally. In this regard, it is expected that the C_1^0(As) center would be differentiated by exhibiting a superhyperfine interaction with the neighboring As atom (although probably unresolved), whereas the C_1^0(S) would not show this effect. It would be most interesting also to investigate in detail the photoinduced ESR spectra of As_xS_{1-x} glasses which had been isotopically enriched with ^{33}S; in this way, through the sulfur-related hyperfine interaction, disulfide bonds should be more readily identifiable.

However, the ESR characteristics of the P_2^0(2S) (As_I) center is expected to be different from that of the P_2^0(As,S) (As_{II}) center; in the latter case, the unpaired electron is predicted theoretically to be very strongly localized in an As *p*-like NBO state, whereas in the former case, the appreciable degree of π bonding between the NBO's of the As dangling bond and the neighboring Se atom would lead to a significantly increased degree of delocalization of the unpaired spin.[11] Experimentally, it is claimed, from the results of the fitting of the ESR line shape, that the electron spin in the As_I center is indeed more delocalized than in the As_{II} center.[5] Based on the fitting results of a previous study of ESR centers in *a*-As_2O_3,[18] Hautala, Ohlsen, and Taylor[5] also state that the As_I center is appreciably more *s-p* hybridized than is the

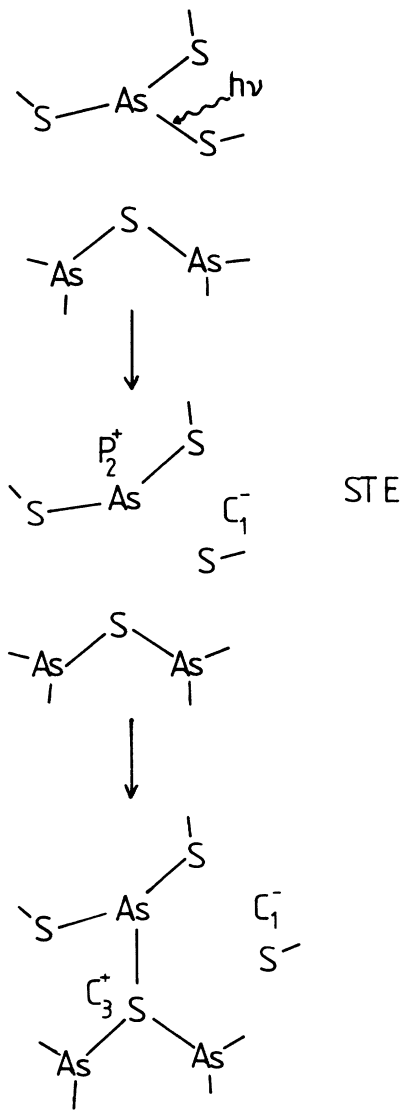

FIG. 3. Defect-transformation mechanism for the conversion of a P_2^+-C_1^-, self-trapped exciton (STE) state into a metastable C_3^+-C_1^- configuration involving intermolecular ("interlayer") bond switching.

As_{II} center. However, owing to the ambiguity over the sign of the $A_\perp$ component of the axially symmetric hyperfine tensor, the degree of localization and the character of the wave function are somewhat uncertain. Either the wave function is localized almost entirely on the As atom, with values of the s and p wave-function coefficients, $c_s^2=4\%$ and $c_p^2=96\%$ (with $A_\perp$ assumed to be negative, as in Ref. 18), or only about 40% of the wave function is on the As atom, with this portion composed of 3% s character and 36% p character, the remaining 60% of the wave function presumably being associated with the surrounding chalcogen ligands, if $A_\perp$ is assumed to be positive.[19] In our interpretation of the As_I center, in terms of a $P_2{}^0(2S)$ defect, the extent of s-p hybridization is expected to be approximately as small as that of the $P_2{}^0(As,S)$ (As_{II}) center, and so we favor the choice of a negative $A_\perp$, as in Ref. 18.

It should be mentioned at this juncture that the ESR signature of the strongly s-p hybridized center $P_4{}^0$ is not consistent with that observed experimentally for As_I centers. Gaczi[4] has shown that this center should exhibit a characteristic four-line ESR spectrum, which is completely unlike that observed experimentally.

Finally, in this discussion of likely candidates for LESR centers in glassy As_xS_{1-x}, we comment on the fact that the concentration of light-induced type-I defects (As_I and S_I) appears to be practically *independent* of composition (x).[5] This feature can be understood by noting that, in our identification of these centers, the defects responsible [$C_1{}^0(P)$ and $P_2{}^0(2C)$] are formed mainly from (a subset of) the products of the photoinduced bond breaking of heteropolar bonds in those chemically ordered parts of the structure far from homopolar bonds [Fig. 1(a)]. (Direct homopolar bond breaking also leads to these products [Figs. 1(b) and 1(c)], but in a much smaller proportion.) The observed virtual independence of the type-I LESR density with composition[5] (in the range of $0.3<x<0.43$) is then understandable, since for this range of compositions the concentration of heteropolar bonds, and hence the probability of creating $P_2(2C)$ and $C_1(P)$ defects, changes rather little. Of course, the proportion of heteropolar bonds is expected to be highest for the stoichiometric composition ($x=0.4$), and it may therefore be significant that, indeed, the concentration of type-I LESR centers for a-As_xS_{1-x} does appear to exhibit a small maximum at this composition.[5]

IV. CONCLUSIONS

We have discussed in detail for the first time the microscopic processes which lead to the creation of paramagnetic centers responsible for light-induced ESR (LESR) in amorphous chalcogenides. We show that the presence of homopolar (wrong) bonds is essential in these compound materials for the optically induced creation of metastable paramagnetic dangling-bond defects, but the creation process does not involve the scission of such homopolar bonds themselves. Finally, it should be stressed that, although the photoinduced bond breaking is invoked to explain the LESR results,[2–5] and our results on photoinduced changes in the photoconductivity[8] and ac conductivity,[6,7] such processes do not account for all photoinduced phenomena in amorphous chalcogenides. In particular, photodarkening most likely results from changes in interchain interactions not involving covalent bond breaking.[12,20]

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