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Direct evidence of three-center Auger recombination processes in ZnS:Cu,Fe

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The existence of the process of nonradiative recombination of an electron on a donor with a hole on an acceptor, caused by energy transfer to a neighboring iron center followed by iron ionization, is proved directly by means of the electron-spin-resonance technique.

There is a rapidly growing amount of data on the role of Auger processes in nonradiative recombination of excitons (e.g., Refs. 1 and 2) and donor-acceptor pairs (DAP's),[3-5] and in intracenter transitions.[6-8] In all these cases, radiative recombination is quenched due to energy transfer to either free or loosely bound carriers. As far as "deep" impurities are concerned, their role in Auger processes has not really been determined.

The question of energy transfer between recombining DAP's and transition-metal (TM) impurities has been considered in the paper of Tabei, Shionoya, and Ohmatsu.[9] These authors, applying the model of Dexter[10] and Schaffer and Williams,[11] have proved that for ZnS:Cu,Mn the quenching of Cu-related photoluminescence (PL) can be explained by an energy transfer to Mn ions, leading to Mn intracenter excitation. For the other TM impurities studied (iron, cobalt, nickel) it has been concluded that some other mechanism must be dominant, and the role played by the energy-transfer processes remains unclear.

An interesting conclusion has been drawn from recent studies of the nonradiative recombination processes in iron-doped ZnS:Cu.[12] It has been proposed that Cu-related DAP emission can be reduced, due to energy transfer from recombining DAP's to iron centers, which are ionized in this process. Such a process would proceed as follows: First, the Cu-related acceptors are ionized by light. At low temperatures the electrons thus induced in the conduction band (CB) are captured mostly by shallow donor centers and DAP recombination results in the visible PL of ZnS. Some of the pairs can, however, recombine nonradiatively, due to transfer of energy to nearby iron centers. It has been postulated that, instead of inducing an intracenter excitation (as in the case of Mn), iron is ionized as a consequence of such an energy transfer. Such a process, which can be called a three-center (donor, acceptor, and, in our case, iron) Auger recombination (TCAR), has previously been considered by Kudykina, Tolpygo, and Sheinkman[13] for DAP's and a recoil particle bound to a shallow donor or an acceptor.

The role of the deep centers in TCAR has remained practically unknown. Only in the case of lightly-oxygen-doped GaP has it been postulated that the deactivation of infrared PL at low temperatures is due to the TCAR process involving an oxygen-related deep donor.[14] Some indirect data also indicate that TCAR may be responsible for the quenching of a visible PL and for inducing orange and infrared emissions in CdI_2 (Ref. 5) and CdS,[15,16] respectively.

This Rapid Communication is devoted to showing directly that a TCAR process involving the iron impurity in the ZnS is an efficient nonradiative recombination channel in this lattice. To prove this we should show that DAP recombination is accompanied by ionization of some of the iron centers in the sample from the Fe^{2+} charge state, occupied "in the dark," to the Fe^{3+} state, and that this can be accounted for only by the energy-transfer process. First, it should be emphasized that this could not be done convincingly by means of standard optical methods, which probably explains why no evidence of TCAR has been reported. This is because the Fe^{3+} ion and the free electron created in this process then recombine mostly nonradiatively. It has been shown[12] that $Fe^{3+}+e$ recombination proceeds by multiphonon emission to the $^5T_2$ excited state of Fe^{2+}, followed by 3.4-μm ($^5T_2 \rightarrow {}^5E$) emission. Since the 3.4-μm emission is also induced by other recombination transitions, as discussed in Ref. 12, any reliable evidence of the TCAR could not be derived by measuring, e.g., the 3.4-μm PL excitation spectrum.

A new experimental approach to the energy-transfer phenomena is proposed here. As has been explained above, as a consequence of the TCAR, iron should be ionized, i.e., the Fe^{3+} state ($3d^5$ configuration with the $^6S_{5/2}$ ground state) should be induced, which is easily detected by means of the electron-spin-resonance (ESR) technique. Therefore, we propose that TCAR can be simply verified by ESR, which is a sensitive way of measuring *s*-state centers and their excitation spectra (photo-ESR).

The photo-ESR experiments have been performed on a standard ESR spectrometer (Bruker B-ER 418s), equipped with a simple optical set for *in situ* sample illumination. High-pressure xenon (150 W) and mercury (200 W) lamps, with either interference filters or a simple monochromator, have been used for ESR signal excitation. All the other details of sample preparation and experimental methods and equipment can be found elsewhere.[12,17,18]

The method of showing, by ESR, that TCAR exists, is quite simple. We should measure the Fe^{3+} signal excitation spectrum for acceptor-codoped samples (Cu in our case) and compare it with that measured for only iron-doped samples. The $Fe^{2+} \rightarrow Fe^{3+}$ direct photoionization transition ($Fe^{2+}+h\nu \rightarrow Fe^{3+}+e_{CB}$; e_{CB} is an electron in the conduction band) and its spectral dependence has already been measured in detail,[12,18] which makes such an approach reliable. We should prove that iron is efficiently ionized in the excitation energy range in which the acceptors are ionized, i.e., DAP recombination is induced. Therefore, the first step in our procedure should be a verification of the acceptors present in the crystals studied, and of their ionization transitions. This can also be easily done by means of the ESR technique, as explained in detail in Ref. 17. Here, we have utilized the fact that the valence band (VB) → acceptor and acceptor → CB complementary photoionization transitions can be monitored by a change of the intensities of the ESR signals of the deep centers (Cr,Fe), caused by partial recapture by these deep centers of the free carriers thus generated in the CB, VB. It should be emphasized that a typical contamination of ZnS samples with chromium ($\sim 10^{16}$ cm^{-3}) has allowed us to obtain more reliable information on acceptor centers. By performing similar measurements on the Fe^{3+} and Cr^{+} ESR signals, we could unambiguously check which free carriers are generated in a given process either in CB or VB.

The experimental results obtained by studying acceptors photoionization transitions are summarized in Fig. 1. It has been found that at least three different types of acceptor states exist in our samples, with their energy levels localized above the top of the VB as follows: 0.75 eV for the acceptor labeled $A1$, 1.0 eV for the acceptor labeled $A2$, which we relate to the zinc-vacancy–donor (V_{Zn}-D) pairs, and 1.25 eV for the acceptor labeled $A3$, which is most probably copper related. The above means that, in addition to the intentionally introduced Cu-related acceptors, the so-called A center (V_{Zn}-D) acceptors are present in our samples, as is also the case for other ZnS crystals. The data shown in Fig. 1 mean that acceptors are ionized (DAP recombination is induced) for $h\nu > 2.6$ eV ($A3$ acceptor), 2.8 eV ($A2$ acceptor), and 3.1 eV ($A1$ acceptor).

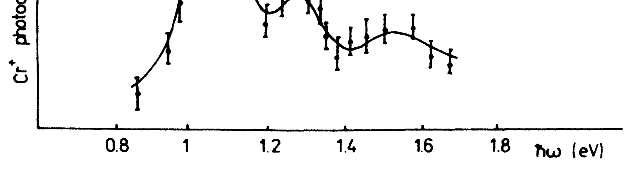

FIG. 1. The photoionization absorption spectrum of ZnS:Cu,Fe due to VB → acceptor neutralization processes measured indirectly by means of the photo-ESR technique. In the inset is shown the complementary (acceptor → CB) photoionization spectrum. This spectrum has been obtained by measuring the light-induced concentration of the shallow donor centers, by observing the Cr^{+} ESR signal rise ($Cr^{2+} + e_{CB} \rightarrow Cr^{+}$) and the Fe^{3+} ESR signal decay ($Fe^{3+} + e_{CB} \rightarrow Fe^{2+}$) ($\Delta I_{ESR}$) caused by the capture of electrons thermally released to the CB from these donors.

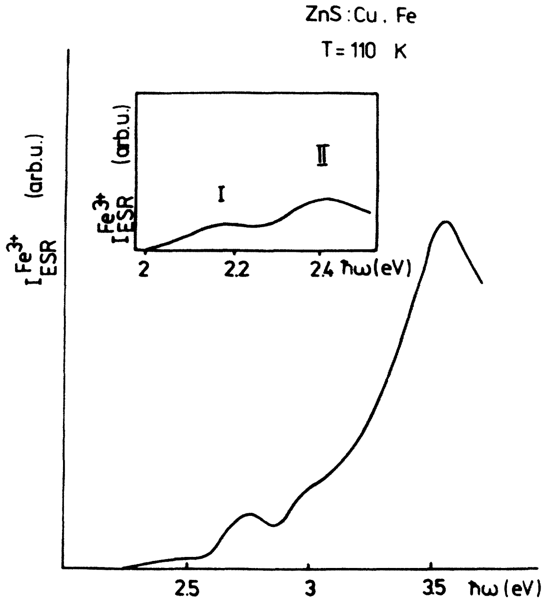

FIG. 2. The spectral distribution of the Fe^{3+} excitation for ZnS:Cu,Fe. A similar dependence has been obtained for the Cr ESR signal.

The excitation spectrum of the Fe^{3+} ESR signal is shown in Fig. 2. It is apparent that, for ZnS:Cu,Fe, Fe^{3+} is induced most effectively for excitation energy $h\nu$ larger than 2.6 eV, i.e., in the energy range in which acceptors present in the crystal studied are ionized. The usually observed bands,[18] which dominate for heavily iron-doped ZnS samples undoped with acceptors (labeled I and II in Fig. 2) due to $Fe^{2+} + h\nu \rightarrow Fe^{3+} + e_{CB}$ direct photoionization (I) and two-step processes, such as $Cr^{2+} + h\nu \rightarrow Cr^{+} + h_{VB}$, $Fe^{2+} + h_{VB} \rightarrow Fe^{3+}$ (II), are fairly small in comparison to these observed for $h\nu > 2.6$ eV.

Before concluding that these data confirm a high efficiency of the postulated TCAR [shown in Fig. 3(b)], other possibilities should first be excluded. These are also shown in Fig. 3: an energy transfer process including two acceptors (a) and a two-quanta excitation process (c). In both

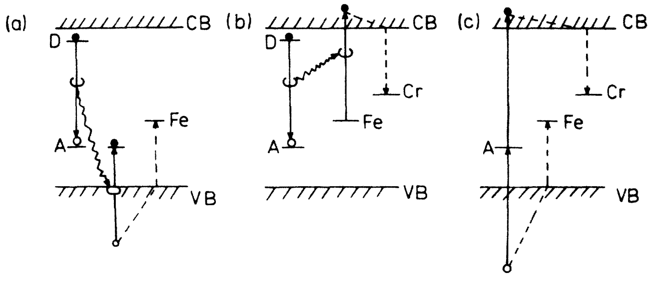

FIG. 3. The possible recombination mechanisms which could account for the Fe^{3+} ESR signal excitation under the illumination which ionizes acceptors: (a) three-center Auger recombination involving a DAP pair and a neighboring ionized acceptor. (b) Three-center Auger recombination process in which iron is ionized due to the energy transfer from recombining a DAP pair. (c) Two-quanta acceptor ionization and neutralization process.

these cases, Fe^{3+} is induced due to a capture of holes created in the VB in the following: (a) TCAR process of a DAP and a nearby acceptor as a third center or (c) due to a high efficiency of two-quanta processes. In the latter case, the first quantum ionizes an acceptor (acceptor → CB transition) and the second induces a complementary photoionization transition (VB → acceptor) before DAP recombination can proceed. Fortunately, we can easily exclude the possibility that Fe^{3+} is induced for $h\nu > 2.6$ eV due to a hole-capture process [(a), (c), or any other process]. This is because for $h\nu > 2.6$ eV illumination we have observed simultaneous excitation of the Fe^{3+} and Cr^{+} ESR signals. As we have checked, the Cr^{+} state has a much larger hole-capture cross section (Coulomb attractive potential) than the Fe^{2+} state and typical acceptors in ZnS. This means that the Cr^{+} ESR signal should be immediately quenched in any of the processes which preferably induce holes in the VB. The simultaneous observation of the Cr^{+} and Fe^{3+} ESR signals for $h\nu > 2.6$ eV illumination can only be explained if iron is ionized in the process, and if some of the electrons induced in the CB are then captured by chromium. This leaves either direct iron ionization or the TCAR process shown in Fig. 3(b) as the only candidates which can explain the Fe^{3+}, Cr^{+} excitation spectra for $h\nu > 2.6$ eV. As has already been mentioned, the first of these processes occurs for $h\nu > 2$ eV and is fairly inefficient (the $Fe^{2+} \rightarrow$ CB process is parity forbidden[18]) as can be seen in Fig. 2. Therefore, we can conclude that simultaneous observation of two ESR signals (Fe^{3+},Cr^{+}) in our ESR experiments has made possible direct confirmation of the high efficiency of the TCAR process. This is a typical situation in photo-ESR studies, in that at least two photosensitive signals should be observed for unambiguous interpretation of the data (see, e.g., Ref. 17).

The strong impact of the TCAR on the Fe^{3+} excitation spectrum need not necessarily mean that this is the dominant mechanism responsible for deactivation of the ZnS visible PL in ZnS:Cu,Fe. We can easily estimate its efficiency utilizing the fact that the TCAR belongs to a wider class of the three-center energy-transfer processes analyzed by Schaffer and Williams.[11] Bearing this in mind, the probability of the TCAR can be estimated from the spectral overlap between the emission spectrum of DAP's and the photoionization absorption spectrum of iron. Based on this it is found that the TCAR process cannot explain more than 10% of the overall efficiency of iron related deactivation of the ZnS:Cu,Fe visible PL. It has been clarified earlier that the main mechanism is the preferential compensation of copper by iron, which leads to Fe^{3+}-Cu^{+} associates.[12] Any more elaborate determination of the TCAR efficiency is difficult to perform, since the theoretical work on this problem does not seem to be sufficiently advanced. The model of TCAR proposed by Kudykina *et al.*[13] relates to the case of relatively shallow donor and acceptor centers. Such a model cannot be readily applied to the TCAR process, in which a fairly deep ZnS acceptor and a "deep center" due to TM are involved.

Until recently, only the direct and the two-step processes have been considered when discussing the spectral dependence of the ESR signal excitation (quenching). Our data indicate that judicious application of the photo-ESR technique can also yield a better understanding of a quite complex energy-transfer mechanism.

We are indebted to J. M. Langer for stimulating discussions on the role of Auger processes in nonradiative recombination transitions.

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