Nature of the native deep localized defect recombination centers in the chalcopyrite and orthorhombic $AgInS_2$

J. Krustok,[a] J. Raudoja, and M. Krunks
Institute of Materials Science, Tallinn Technical University, Ehitajate tee 5, Tallinn 19086, Estonia

H. Mändar
Institute of Materials Science, Tartu University, Tähe 4, Tartu 51010, Estonia

H. Collan
Optoelectronics Laboratory, Helsinki University of Technology, P.O. Box 3000, Espoo, FIN-02015, Finland

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We studied the deep photoluminescence (PL) emission in polycrystalline chalcopyrite and orthorhombic $AgInS_2$. In both phases several PL bands were detected at 8 K. On the energy scale these deep PL bands are positioned according to a regular pattern. This is explained as being due to electron-hole recombination within very close deep donor-deep acceptor pairs, with different distances between donor and acceptor defects. The deep donor defect is an interstitial silver Ag_i and the native deep acceptor defect appears to be situated at the Ag or In place. The two different crystal modifications also cause slightly different distances between donor and acceptor defects in the $AgInS_2$ lattice and, as a result of this, different spectral positions of the deep PL bands. It is shown that these deep localized donor–acceptor pairs can be reasonably efficient radiative recombination centers up to distances of 5.3 Å between the deep donor and the deep acceptor and, thus, up to six distinct deep PL bands are visible in $AgInS_2$. The deep donor-deep acceptor pair model is confirmed also by the temperature quenching experiments and by the excitation power dependences. © *2000 American Institute of Physics.* [S0021-8979(00)01513-9]

I. INTRODUCTION

Ternary chalcopyrite semiconductor compounds, such as $CuInSe_2$ or $CuGaSe_2$, have attracted considerable attention for practical application in thin film solar cells. Therefore the study of their physical properties and defect structure is of great interest. Theoretical calculations have shown that there must be quite deep defect levels in ternaries,[1] but experimentally they are not so often detected. A systematic study of the deep photoluminescence (PL) bands in $CuGaSe_2$ and $CuInS_2$ was done recently.[2] From the experimental information gathered, it was proposed in Ref. 2 that some of these deep PL bands found in $CuInS_2$ and $CuGaSe_2$ can be explained as an electron-hole recombination within donor–acceptor (DA) pairs involving deep donor and deep acceptor levels. Later this picture found additional confirmation by the fact that a whole series of these theoretically predicted deeper PL bands were experimentally detected in $CuInS_2$ and $CuIn_{0.5}Ga_{0.5}S_2$.[3] As the fine structure of these deeper PL bands in $CuInS_2$ was studied in detail,[4] it was concluded that the donor defect in these deep DA pairs is an interstitial copper Cu_i. This immediately raised the question of the possibility of analogous native defects in other related compounds, such as $AgInS_2$. Do we also have an interstitial silver donor Ag_i? Thus it was acutely interesting to look for these same deep PL bands in $AgInS_2$.

$AgInS_2$ is a ternary compound which can exist in two forms: chalcopyrite (space group No. 122) and orthorhombic (space group No. 33).[5–8] The orthorhombic (*o*) form is stable at high temperature ($T>620\,^{\circ}C$) and the chalcopyrite (*c*) form is stable at low temperature ($T<620\,^{\circ}C$).[5,6] Different crystal modifications must also give somewhat different distances between interstitial positions and lattice sites and, according to the deep donor-deep acceptor (DD-DA) model,[2–4] the deep PL bands in the two forms should have an analogous but different structure. In this article we have studied deep PL bands in both crystal modifications of $AgInS_2$.

II. EXPERIMENT

The polycrystalline $AgInS_2$ material was synthesized of 5N-purity components. Ag, In, and S were weighted according to the molar ratios 1:1:2 (with a little deficiency of sulphur, in order to prevent an explosion of the ampoule during the high-temperature treatment), and loaded into the quartz ampoule. The ampoule was evacuated to high vacuum at room temperature. The sealed ampoule with components was heated up to the reaction temperature of 900 °C in a tunnel furnace and held at 900 °C for 5 h. During the next 5 h the temperature was lowered to 860 °C, followed by a cooling of the whole furnace in about 12 h to 250 °C. In order to arrive at the right, stoichiometric composition, the synthesized $AgInS_2$ polycrystalline material was treated in a two-zone ampoule under a sulphur vapor pressure of 0.15×10^5 Pa and with the temperature of the material zone at 700 °C. The ampoule was cooled ''rapidly'' by putting it into a cold water bath. The resulting $AgInS_2$ ingot was broken into pieces for further treatments. The sample pieces were annealed, at either 600 or 700 °C, to establish the chalcopyrite or the

[a]Author to whom correspondence should be addressed; electronic mail: krustok@cc.ttu.ee

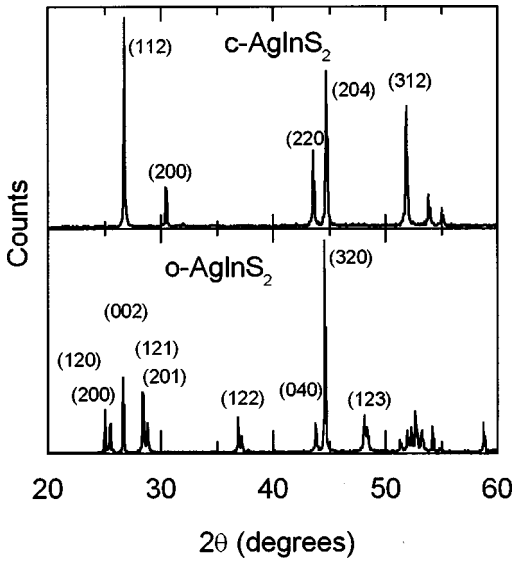

FIG. 1. X-ray diffraction patterns of our polycrystalline chalcopyrite and orthorhombic $AgInS_2$ samples.

orthorhombic structure, respectively. After a 24 h annealing in an evacuated and sealed ampoule both materials were rapidly cooled in cold water.

A He–Cd laser at a wavelength of 441 nm was used as the excitation source for steady-state PL measurements at temperatures ranging from 8 to 300 K. The laser beam was focused onto the sample with a spot diameter of about 100 μm and the luminescent radiation was analyzed with a 0.4 m grating monochromator and detected by either a PbS detector, an InGaAs detector, or a photomultiplier tube with S1 characteristics. All samples were etched prior to measurement in a solution of bromine in methanol in order to ensure good and comparable surface properties.

III. RESULTS AND DISCUSSION

A. Crystal structure

The crystal structure of $AgInS_2$ in both modifications is slightly distorted. This distortion has led to various interpretations of the crystal structure, especially of the orthorhombic phase. The crystallographic properties of our samples were confirmed by the x-ray diffraction (XRD) technique. As shown in Fig. 1, both phases are relatively pure and even the higher-temperature orthorhombic phase does not contain imprints of a low-temperature chalcopyrite phase. Only a small deviation of relative intensities of the XRD peaks exists, compared with the results of Roth, Parker, and Brower,[5] probably caused by the texture of our polycrystalline samples.

The chalcopyrite phase in ternaries is quite common and there are no assignment problems with this phase. There are two types of interstitial positions in the chalcopyrite lattice ($i1$ and $i2$). Taking the unit cell corners to be defined by silver atoms, these interstitial positions have the coordinates (1/2, 1/2, 1/4) and (3/4, 1/4, 1/8), respectively. It is important to realize that atoms at these two interstitials have a different surrounding.

TABLE I. Possible distances between the two interstitial positions ($i1$ or $i2$), and the Ag or In sites, respectively, in the chalcopyrite and orthorhombic lattice of $AgInS_2$. Starting from the shortest one, the distances are labeled D1, D2,... etc.

	Chalcopyrite		Orthorhombic	
No.	Lattice sites	Distance, Å	Lattice sites	Distance, Å
D1	Ag-$i2$,In-$i2$	2.49	In-$i2$,Ag-$i1$	2.48
D2	Ag-$i1$,In-$i1$	2.8	Ag-$i1$,In-$i2$	2.51
D3	Ag-$i1$,In-$i1$	2.91	In-$i1$,Ag-$i2$	3.45
D4	Ag-$i2$,In-$i2$	4.68	In-$i1$,Ag-$i2$	4.8
D5	Ag-$i2$,In-$i2$	4.81	In-$i1$,Ag-$i2$	4.81
D6	Ag-$i1$,In-$i1$	4.98	In-$i1$,Ag-$i2$	5.3
D7	In-$i2$	6.23	In-$i1$,Ag-$i2$	6.26

The related two interstitial positions can also be found in the orthorhombic phase. The structure data of this phase is not included in ICSD single crystal database (Fiz Karlsruhe and Gmelin-Institut, Release 99/1). As the XRD patterns of our orthorhombic samples fit well with the pattern data found in Ref. 5, then we used structure data of Roth, Parker, and Brower in our analysis. Unit cell of orthorhombic $AgInS_2$ (space group $Pna2_1$) contains 16 atoms, all in general Wyckoff position (4a with the following coordinates: Ag at (1/12, 5/8, 0), In at (1/12, 1/8, 0), S at (1/12, 1/8, 1/4), and (1/12, 5/8, 3/8). According to Ref. 6, orthorhombic $AgInS_2$ has a pseudo-wurtzite lattice. Interstitial positions $i1$ and $i2$ have the coordinates (3/4, 1/8, 3/8) and (3/4, 5/8, 3/8), respectively. One should note, however, that the crystal structure of the orthorhombic $AgInS_2$ may need further studies and that, therefore, the true positions of atoms can be slightly different from those proposed by theory.

Assuming that the DD-DA pairs include an Ag_i atom as a deep donor and a deep acceptor at the Ag or In site, we first calculate all possible DD-DA separations in both lattices. We have used the low-temperature values for lattice parameters, $a=5.818$ Å and $c=11.216$ Å for the chalcopyrite phase[9] and $a=6.9995$ Å, $b=8.2553$ Å and $c=6.6847$ Å for the orthorhombic phase.[10] Results of these calculations are given in Table I.

B. Edge emission

The c-$AgInS_2$ and o-$AgInS_2$ have slightly different low-temperature values of the energy gap E_g: 1.918[11] and 2.059 eV[12] respectively. This difference can be clearly observed from Figs. 2 and 3, where the near band edge PL emission spectra of both phases is given. The edge emission of the chalcopyrite $AgInS_2$ can be fitted with 2 PL bands. The high-energy structured band has a zero-phonon line at $E=1.819$ eV, phonon energy $\hbar\omega=37$ meV, and a Huang–Rhys factor $S=1.74$. The second Gaussian band has a peak position at $E=1.697$ eV. The experimentally measured edge emission spectrum of o-$AgInS_2$ can be fitted with three different PL bands. The high-energy band shows a weak phonon structure with phonon energy $\hbar\omega=42$ meV, and a Huang–Rhys factor $S\sim 2$. The zero-phonon line of this band is situated at $E=1.966$ eV. The second asymmetric band has

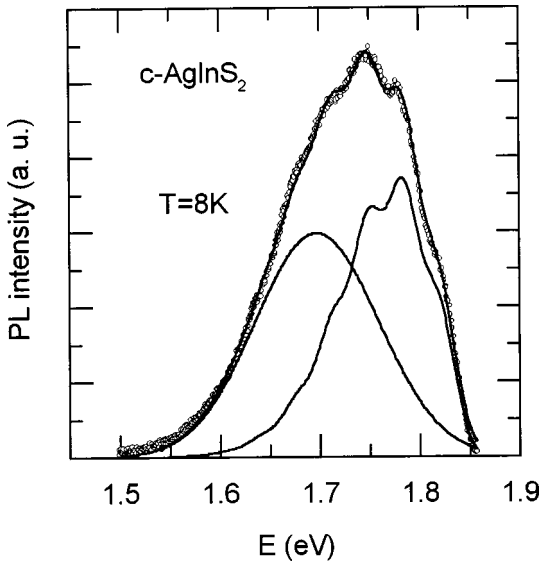

FIG. 2. Experimentally measured edge emission spectrum (dots) of the chalcopyrite $AgInS_2$ and the least-squares fitting results (shown as continuous lines).

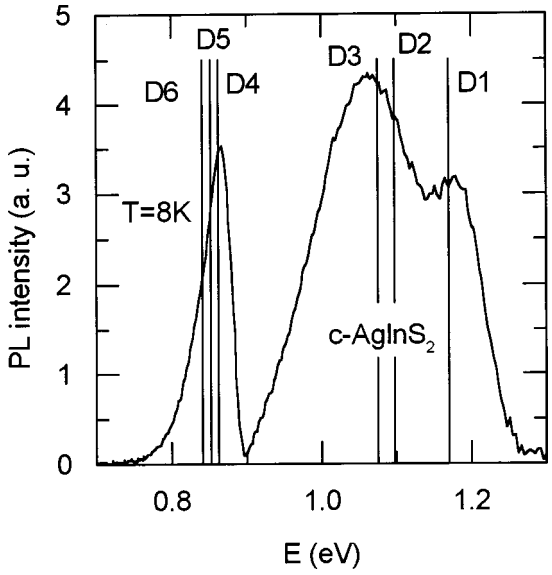

FIG. 4. Experimentally measured deep PL bands in chalcopyritic $AgInS_2$ together with the calculated band positions (indicated by the vertical lines). The dielectric constant value in the calculations was $\epsilon=8.8$.

a peak position at 1.804 eV. At the low-energy side of this edge emission region we may observe also a third wide band with peak position at $E=1.724$ eV.

It is worth noting that corresponding edge emission PL bands in $AgInS_2$ were previously detected in several studies,[11–15] but the chemical nature of defects responsible for these bands remains obscure.

C. Deep PL bands

In the infrared spectral region both phases show several deep PL bands, see Figs. 4 and 5. We notice that the structure of these bands is very reminiscent of those observed previously in $CuInS_2$[2,3] and therefore we assume that the same generic DD-DA model holds in $AgInS_2$, too. According to this model these deep PL bands are a result of a electron-hole recombination within close donor–acceptor pairs, with different separations. It is known that the electron (hole) wave functions in the deep donor (acceptor) level must be highly localized. Because of this, for more distant pairs, there is neither practically any overlap of the initial and final state wave functions and, as a result of this, nor observable recombination emission. It seems to be a reasonable assumption that both the donors and the acceptors can occupy only few energetically favorable positions within the crystal. Then it is possible to calculate, using Table I, the

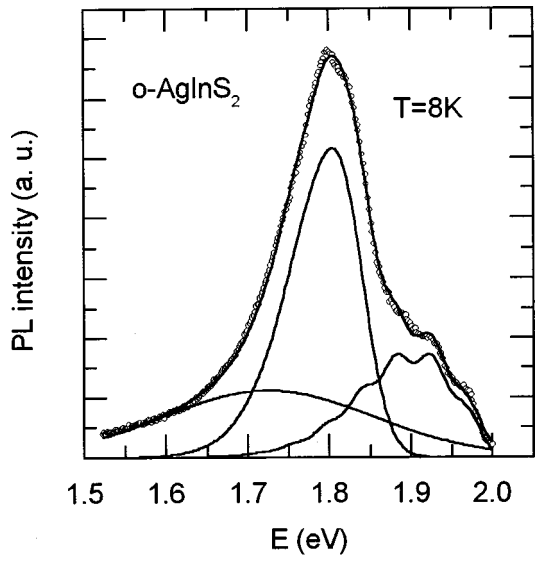

FIG. 3. Experimentally measured edge emission spectrum (dots) of the orthorhombic $AgInS_2$ and the least-squares fitting results (shown as continous lines).

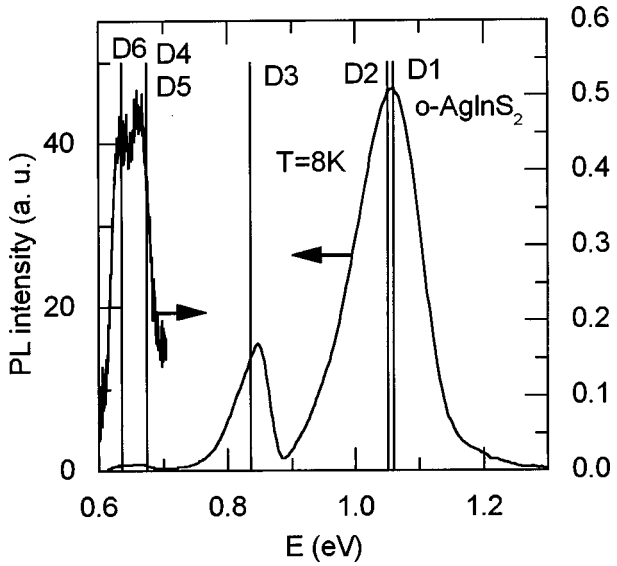

FIG. 5. Experimentally measured deep PL bands in orthorhombic $AgInS_2$ together with the calculated band positions (indicated by the vertical lines). The dielectric constant value in calculations was $\epsilon=7.3$.

approximate energy difference ΔE between the DA pair emissions for the shortest and the next-shortest DA separation, r_1 and r_2, respectively[2–4]

$$\Delta E = \frac{e^2}{\epsilon}\left(\frac{1}{r_1} - \frac{1}{r_2}\right). \quad (1)$$

Here ϵ is the dielectric constant. A similar calculation can be done with more distant pairs with DA separations r_3, r_4, r_5 and so on. In Ref. 2 we calculated, using Eq. (1), all possible energy separations ΔE for donor–acceptor pairs and compared them with the experimentally measured deep PL band positions in $CuInS_2$ and $CuGaSe_2$. These calculations indicated that in those materials the observed deep PL bands must be related to such DA pairs where one of the components is located at an interstitial position. Later we have shown that this interstitial defect is Cu_i, a deep donor.[3,4] Analogously, in $AgInS_2$ the deep donor defect should be Ag_i and we are also tempted to assume that the acceptor defect is situated in the Ag or In sites of the $AgInS_2$ lattice. In order to calculate possible emission energies of corresponding PL bands, one must know the value of dielectric constant ϵ. In compound semiconductors, it is obvious that ϵ must be a combination of both optical and static dielectric constants (i.e., $\epsilon_\infty < \epsilon < \epsilon_0$), but the precise numerical value for it is hard to predict. The second open question is the position of the PL band corresponding to the closest DD-DA pair separation, i.e., of the D1 band. We determined experimentally the D1 band position from the measured PL spectra. For the ΔE calculation, we chose such an ϵ value as to get the best correspondence between experimental observation and the theoretical positions. For the chalcopyritic phase the value we used was $\epsilon = 8.8$, for the orthorhombic phase $\epsilon = 7.3$. The band positions calculated in this fashion are also given in Figs. 4 and 5 as vertical lines.

As can be seen from Figs. 4 and 5, the match between the experiment and theory is quite good. In both phases six different deep PL bands can be observed. According to Table I, the largest distance between the donor and the acceptor, and still showing substantial recombination, is D6 which, according to Table I, in the orthorhombic phase corresponds to a distance of 5.3 Å. Despite the good overall match there is still some disagreement between the experimental and the theoretical emission energies. One must remember that we did not take into account the actual size and the electric charge distribution of the atoms in our calculations. It is apparent that in the real crystal the size and the ''shape'' of the atoms lead to an additional deformation of the lattice and change the theoretically calculated separations.

The D1 band position is 1.17 eV in c-$AgInS_2$ and 1.06 eV in o-$AgInS_2$, respectively. This means that in the orthorhombic phase at least one of the components of the corresponding DD-DA pair has a considerably deeper electronic energy level than in the chalcopyritic phase.

It is a well established fact that, as a rule, the recombination rate of DA pairs increases with decreasing the separation between donors and acceptors. This fact usually leads to the well-known j-shift of the DA PL bands, when the PL band maximum shifts towards higher energy with increasing laser power because more distant pairs saturate more easily.

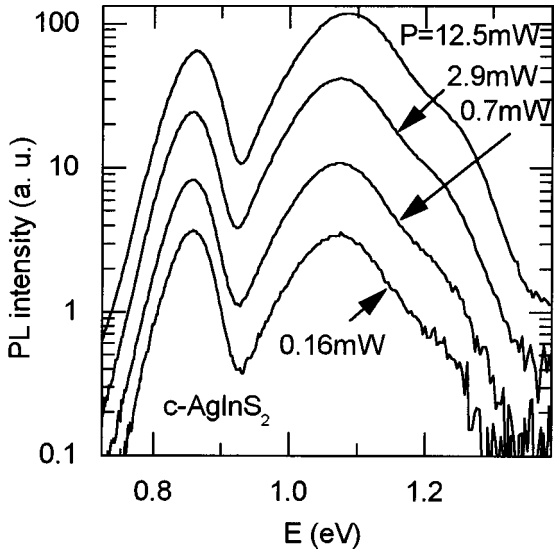

FIG. 6. The PL spectra of chalcopyritic $AgInS_2$ measured for different levels of laser excitation power $P_{ex} = 0.16$–12.5 mW. The intensities of the higher energy PL bands increase faster with P_{ex} than those of the lower energy PL bands, but the positions of the bands do not shift in energy, i.e., there is no j shift of any individual band.

Therefore the relative intensity of the closer-pair PL bands, situated at higher energy, should increase with laser power. We studied this process in our c-$AgInS_2$ samples, see Fig. 6. It is clearly visible that the intensity of the higher energy PL bands increases more quickly with the laser excitation power and that no shift of the actual peak positions can be seen. This fact gives strong credence to our DD-DA model.

It is also known[16] that, due to the Coulombic interaction term $e^2/\epsilon r$, the acceptor (donor) level tends to move closer to the valence (conduction) band when paired with a donor (acceptor) defect. Therefore, the acceptor level of the DD-DA complex having the shortest distance between the donor and the acceptor is expected, as compared with the simple model of Eq. (1), to be situated closer to the valence band edge than for the larger distance complexes. Thus, assuming that the temperature quenching of these DD-DA PL bands is mainly caused by the ionization of the acceptor level, we can predict that the intensity of higher energy PL bands should decrease more rapidly with temperature than the lower energy PL bands. This is exactly what we have observed, see Fig. 7.

IV. CONCLUSIONS

A straightforward photoluminescence study of polycrystalline $AgInS_2$ was performed, with excitation at $E = 2.81$ eV and with radiation detection over a wide energy range, from 0.7 to 1.9 eV. The study revealed several deep emission bands, the energies of which followed a regular pattern. Both in the orthorhombic $AgInS_2$ and in the chalcopyritic $AgInS_2$ six such bands were detected. The relative energies of all these emission bands were fully explained by a deep acceptor-deep donor model, which has the donor component of the pair at an interstitial lattice position and the acceptor component at a metal ion (i.e., either Ag or In) lattice site. The energy difference between the bands was

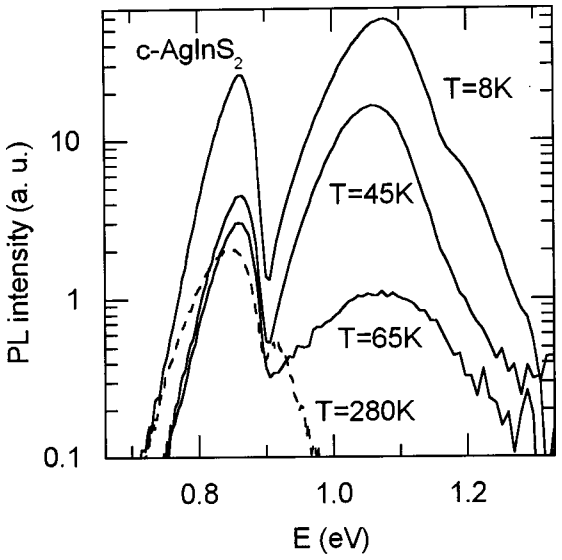

FIG. 7. The PL spectra of chalcopyritic $AgInS_2$ measured at different temperatures $T=8$, 45, 65, and 280 K. The intensities of the higher energy PL bands are seen to decrease faster with T than those of the lower energy PL bands, in full accordance with the present donor–acceptor pair model of close pairs.

found to be caused by the Coulombic interaction term $e^2/\epsilon r$ of singly charged, close DA pairs, as would be the case for the occupied donor level and the vacant acceptor level being neutral, immediately prior to the process of recombination.

The overall deep band structure for $AgInS_2$ was closely similar to the structure observed previously in $CuInS_2$ and in $CuGa_{0.5}In_{0.5}S_2$ in which cases the deep donor was a Cu_i atom. In analogy with this, we conclude that in $AgInS_2$ the deep donor is an Ag_i atom. Thus it would seem that the ternary chalcopyrite semiconductors and related compounds, such as $AgInS_2$, have a pronounced tendency to form such deep native electron-hole defect recombination centers. Because these deep defect states are strongly localized, the luminous efficiency for the very closest donor–acceptor pairs only is substantial. In the present work on $AgInS_2$ no recombination emission for these deep defect pairs further apart than 5.3 Å was detected. There remains the experimental challenge of studying these native defects in more detail and, for instance, in finding out whether the Ag_i atom of these complexes is equally mobile as the Cu_i atom, for instance, is reported to be in the $CuInSe_2$ compound.

ACKNOWLEDGMENTS

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