



Mechanism of Persistent Luminescence in Eu^{2+} and Dy^{3+} Codoped Aluminate and Silicate Compounds

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A mechanism of persistent luminescence that was proposed in 1996 for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+};\text{Dy}^{3+}$ has been widely adopted to explain afterglow in many Eu^{2+} and Dy^{3+} codoped aluminates and silicates. The mechanism involves the thermally activated release of a hole from Eu^{2+} in its excited 5d state to the valence band which is subsequently trapped by Dy^{3+} . In this work the location of the lanthanide energy levels relative to the valence and conduction band of various compounds is presented. It is shown that the mechanism of persistent luminescence cannot be correct. An alternative model that involves the ionization of the 5d electron to conduction band states and subsequent trapping by Dy^{3+} is proposed. The level schemes are consistent, both qualitatively and quantitatively, with many observations regarding persistent luminescence. They also provide insight into the mechanism of thermal quenching of Eu^{2+} 5d-4f emission.

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The first report on the persistent luminescence properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+};\text{Dy}^{3+}$ and $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+};\text{Dy}^{3+}$ was by Matsuzawa *et al.*¹ Eu^{2+} is the recombination center leading to an emission due to the 5d-4f transition. Based on previous studies by Abbruscato on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$,² the following mechanism was proposed. After excitation of Eu^{2+} to the 5d state, a hole is released to the valence band that is subsequently trapped by Dy^{3+} . Thermally activated release of the hole from Dy^{4+} and recombination at Eu^{2+} then leads to the persistent luminescence. This mechanism was further supported by thermoluminescence glow peak analysis by Nakazawa and Machida³ and by Yamamoto and Matsuzawa,⁴ and since then it has been widely adopted in numerous papers without much further questioning about its validity.⁵⁻⁹

Since the work by Matsuzawa *et al.*¹ many other compounds based on the simultaneous doping of Eu^{2+} and Dy^{3+} were found to exhibit intense persistent luminescence, *i.e.*, BaAl_2O_4 ,¹⁰ $\text{CaSrAl}_2\text{SiO}_7$,¹¹ $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$,¹²⁻¹⁵ $\text{M}_3\text{MgSi}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$),^{16,17} $\text{M}_2\text{MgSi}_2\text{O}_7$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$),¹⁸⁻²³ $\text{CaMgSi}_2\text{O}_6$,^{20,24} $\text{Sr}_2\text{ZnSi}_2\text{O}_7$,²⁵ and $\text{CaAl}_2\text{Si}_2\text{O}_8$.²⁶ For each of these compounds the model of Matsuzawa *et al.*¹ is used to explain the mechanism. Experiments to elucidate the mechanism by means of thermoluminescence,^{3,4} electron paramagnetic resonance (EPR),¹⁴ and photoconductivity^{1,2,5} were all interpreted in support of that mechanism. Hölsa and co-workers²⁷⁻³² are some of the few who disagree with the mechanism. They find it unacceptable, with valid arguments, that Eu^{2+} and Dy^{3+} (or Nd^{3+}) are regarded as stable defects in the persistent luminescence mechanism. Very recently an X-ray absorption near edge structure (XANES) spectroscopy study was performed on $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$ by Qi *et al.*³³ The results did not reveal any evidence for the creation of Eu^{3+} nor Dy^{4+} and they concluded that the mechanism of persistent luminescence is still open to question.

Meanwhile, the mechanism of Matsuzawa *et al.* also gained popularity to explain Eu^{2+} 5d-4f luminescence quenching in the electroluminescence phosphors CaGa_2S_4 and SrGa_2S_4 . Najafov *et al.*³⁴ conclude that quenching in $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ is caused by release of a hole from Eu^{2+} to the valence band. Later Chartier *et al.*³⁵ proposed the same mechanism for $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$.

In mechanisms of persistent luminescence, luminescence quenching, and electroluminescence, the thermally activated ionization or field ionization of either electrons to the conduction band or holes to the valence band is an important aspect. To understand these mechanisms it is necessary to accurately know the location of the impurity states relative to the conduction band and the valence band. The problem is that hitherto this information has not been available, leading to mechanisms that rely on speculative ideas.

Recently new methods have become available that make it pos-

sible to determine the absolute location of the lanthanide impurity levels. In this work we apply these methods to reconsider the mechanism of persistent luminescence and luminescence quenching. It is shown that the mechanism proposed by Matsuzawa *et al.* for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+};\text{Dy}^{3+}$ cannot be correct and therefore also the widely adopted explanation of persistent luminescence in many other Eu^{2+} and Dy^{3+} codoped aluminates and silicates. Instead of hole transport via the valence band it is shown that the mechanism must involve electron transport. Eu^{3+} and Dy^{2+} are the stable defects and not Eu^{2+} and Dy^{4+} .

Results and Discussion

Level schemes for CaGa_2S_4 and SrAl_2O_4 .—The method to determine the absolute location of the lowest 4f state and the lowest 5d state of divalent and trivalent lanthanide ions in compounds was presented in detail in previous papers and is not repeated here.^{36,37} Instead only the information used to construct the level schemes in the electroluminescence phosphor CaGa_2S_4 and the persistent luminescence phosphor SrAl_2O_4 is presented.

Recently Bessiere *et al.*³⁸ determined the level scheme for CaGa_2S_4 . The result is reproduced in Fig. 1 where zero energy is at the top of the valence band. $E^{\text{ex}} = 4.35$ eV is the energy of exciton creation, *i.e.*, a bound electron-hole pair. The energy E_{VC} needed to create a free electron in the conduction band is at 4.9 eV. The lowest 4f and lowest 4f5d levels of the divalent and the trivalent lanthanides are drawn in the scheme as function of the number n in the $4f^n$ state of the trivalent lanthanide. SrGa_2S_4 has the same crystal structure as CaGa_2S_4 and also approximately the same bandgap value. We therefore regard the level scheme for CaGa_2S_4 also as representative for that of SrGa_2S_4 .

Ultraviolet and vacuum ultraviolet (VUV) studies by Kamada *et al.*³⁹ reveal the onset of the fundamental absorption in SrAl_2O_4 at $E^{\text{fa}} = 6.50$ eV (191 nm) and the maximum of electron-hole pair creation at $E^{\text{ex}} = 6.9$ eV. Adding the energy of electron-hole binding, we estimate the bottom of the conduction band at $E_{\text{VC}} = 7.4$ eV. We have used these values in the scheme of Fig. 2. The following information was used to further construct the scheme. Yb^{2+} does not show 5d-4f emission (see arrow 1 in Fig. 2), even at 4 K.⁴⁰ This has been explained by an autoionization of the 5d electron and it implies that the 5d state of Yb^{2+} is very close to or inside the conduction band.⁴¹ In Fig. 2 we have placed the lowest Yb^{2+} 5d level at the conduction band bottom at 7.4 eV, and from that the lowest 5d states for each other divalent lanthanide can be placed.³⁶ The energy for the first 4f-5d transition in Eu^{2+} is found at $E_{\text{fd}}(\text{Eu}) = 2.75$ eV (450 nm)^{1,14} (see arrow 2 in Fig. 2). This information is sufficient to place the lowest $4f^n$ state in the scheme for each divalent lanthanide ion.

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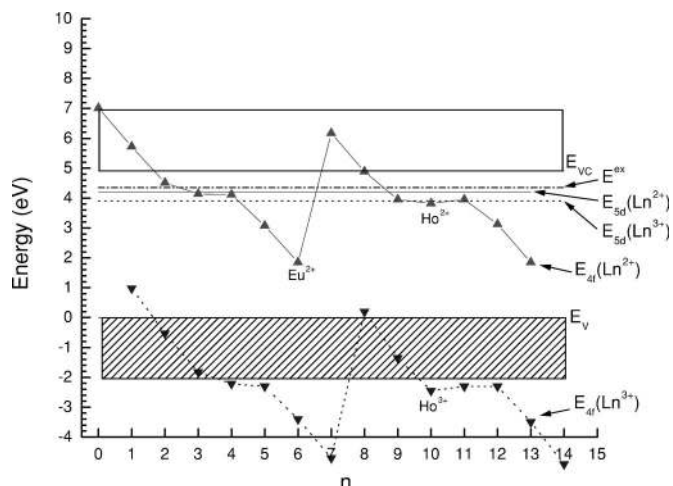


Figure 1. Lanthanide level scheme in CaGa_2S_4 .

Information on the first 4f-5d transition of trivalent lanthanides in SrAl_2O_4 was not found. Therefore we estimate this energy for Ce^{2+} with the relation

$$E_{\text{fd}}(\text{Eu}) = 0.64E_{\text{fd}}(\text{Ce}) + 0.53 \text{ eV} \quad [1]$$

from Ref. 42 and obtain $E_{\text{fd}}(\text{Ce}) = 3.47 \text{ eV}$ (see arrow 3 in Fig. 2). One should further require that the lowest 5d state of trivalent lanthanides should be below those of divalent ones because of a stronger coulombic attraction in the more positive ion. In wide-bandgap BaF_2 , CaF_2 , SrF_2 , and YPO_4 compounds energy differences of around 1 eV were found,³⁶ and in the small-bandgap compound CaGa_2S_4 the difference is reduced to about 0.4 eV (see Fig. 1). For SrAl_2O_4 we estimate a value of around 0.7 eV (see arrow 4 in Fig. 2). With this information all the levels for the trivalent lanthanides can be drawn in the scheme.

In constructing the scheme we did not distinguish between the various Sr sites that can be occupied by the lanthanide impurities. Obviously, the level locations for the lanthanides at different sites may be slightly different. At this moment we should treat the scheme for SrAl_2O_4 as a first estimate of the level positions, and it is well possible that the levels especially for the trivalent lanthanides may shift $\pm 0.5 \text{ eV}$. Despite these possible systematic errors, the schemes still give a proper account on how level posi-

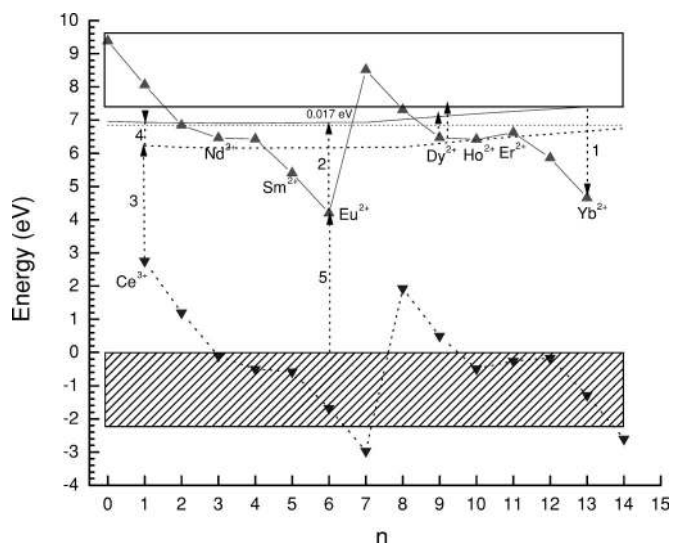


Figure 2. Lanthanide level scheme in SrAl_2O_4 .

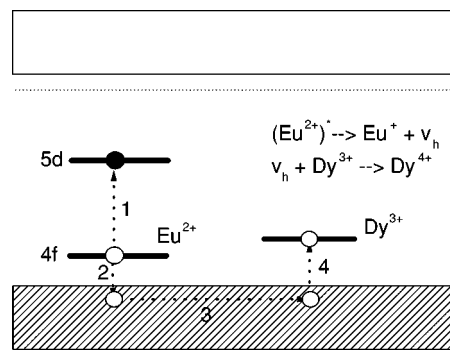


Figure 3. The mechanism of persistent luminescence based on hole release to the valence band.

tions change with the type and charge of the lanthanide ion. They prove accurate enough to deny the mechanism of Matsuzawa *et al.*¹ and to propose an alternative one consistent with experimental observations.

Both schemes show a characteristic variation of the lanthanide ground state energy with the number of electrons in the 4f state. The binding is large in the half and fully filled 4f shells and small when the 4f orbital is filled with one or eight electrons. The binding in the trivalent lanthanides is about 6 eV stronger than in the divalent ones because of the stronger coulombic attraction by the more positive ion. The difference is much smaller ($< 1 \text{ eV}$) for the 5d electrons because they orbit further from the positive core. Furthermore, shielding effects by surrounding anions may also play a role. The energy of the 5d state is relatively invariant with the number of electrons in 4f. In wide-bandgap oxides and fluorides it was found that the 5d state of Yb^{2+} is always about 0.5 eV higher than that of Eu^{2+} ,⁴¹ but in smaller bandgap and more polarizable sulfides like CaGa_2S_4 the 5d state seems to be rather constant.³⁸

Mechanism of persistent luminescence.—Figure 3 shows the widely adopted mechanism of persistent luminescence as originally proposed by Matsuzawa *et al.*¹ Excitation of Eu^{2+} to the 5d state by ambient light (arrow 1) is followed by thermally activated release of “the hole” on 4f to the valence band (arrow 2). The energy barrier for thermal activation is 0.017 eV.^{1,4} The hole migrates through the valence band (arrow 3) until it is trapped by Dy^{3+} with a trapping depth of about 1 eV^{4,14} (see arrow 4). The reversed route is followed to produce the afterglow. Note that Eu^+ and Dy^{4+} are regarded as the stable valencies.

The valence and conduction band levels are delocalized Bloch states, and excitation of an electron from the valence band to the conduction band leads to a “real hole” in the valence band, *i.e.*, a hole that can accept an electron. The $4f^n$ and $4f^{n-1}5d^1$ states of the lanthanide ions are localized impurity states. After excitation of Eu^{2+} to the 5d state one may not interpret the 4f state in Fig. 3 as a hole state that can be filled by another electron. The transition indicated by arrow 2 in Fig. 3 is therefore impossible and based on a wrong concept of a hole state. One can only treat it as a real hole state after the electron has been completely removed from the lanthanide, in other words, when the electron is delocalized and Eu^{2+} has been converted to Eu^{3+} .

The energy needed to excite a hole from Eu^{2+} to the valence band is the same as the energy needed to excite an electron from the valence band to Eu^{2+} and ending in the ground state of Eu^+ . This state is similar to that of the free Eu^+ ion and is formed by the $4f^75d$ configuration. Because the binding energy in the lowest 5d state decreases from Eu^{3+} to Eu^{2+} to Eu^+ , the 5d state of Eu^+ is expected at higher energy than the 5d state of Eu^{2+} . This means that it must be close to or above the bottom of the conduction band in Fig. 2. The energy needed to release a hole from Eu^{2+} in its lowest 5d state is

then larger than $E_{VC} - E_{fd} = 4.6$ eV, which fully disagrees with the 0.017 eV activation energy in the mechanism proposed by Matsuzawa *et al.*

The above reasoning shows that the widely adopted mechanism of persistent luminescence is based on the wrong presumption that there is a hole on Eu^{2+} after it has been excited to the 5d state. Also, the idea that Eu^+ is created in the process cannot hold because it requires too much energy. The experimental evidence that holes are the charge carriers in the persistent luminescence mechanism is based on two reports only. Abbruscato² reports that Hall-effect measurements on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ with excess of alumina shows that holes are the conductive species. Because the decay times of the persistent luminescence and photoconductivity are similar, that would indicate that the same charged species, in this case holes, is responsible for both phenomena. Matsuzawa *et al.*¹ report that the photocurrent in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ under illumination in the vicinity of the negative electrode is more than three times higher than that in the vicinity of the positive electrode. According to Matsuzawa *et al.* this clearly indicates that the charge-carrying species is a hole. In the author's opinion the results of these two reports do not provide solid evidence that holes are the charge carrier in the persistent luminescence mechanism. Much more detailed investigations are needed to obtain rigorous evidence. Clearly, the model of persistent luminescence has to be reconsidered and one should be open to alternative mechanisms and charge carriers. The same applies to the model proposed by Najafov *et al.*³⁴ and Chartier *et al.*³⁵ to explain thermal quenching of Eu^{2+} 5d-4f emission in SrGa_2S_4 and CaGa_2S_4 .

The level schemes suggest an alternative mechanism. Ambient light excites the 5d state of Eu^{2+} . By means of thermal activation the 5d electron is excited to the conduction band and Eu^{3+} is formed. The energy barrier of 0.017 eV is now interpreted as the energy difference between the lowest 5d state and the bottom of the conduction band. It agrees well with the scheme in Fig. 2. Next the electron is trapped in Dy^{3+} to form Dy^{2+} . The scheme shows that the ground state of Dy^{2+} is located 0.9 eV below the bottom of the conduction band, and this value agrees with the trap depth of about 1 eV derived from thermoluminescence studies by Yamamoto and Matsuzawa⁴ and Nag and Kutty.¹⁴ An electron-trapping model was also suggested by Yuan *et al.*⁵ However, they rejected it because at that time holes were believed to be the transporting charge carriers.

The level schemes are consistent with many other observations. Nakazawa and Machida³ and Yamamoto and Matsuzawa⁴ studied the persistent luminescence mechanisms in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ with different trivalent lanthanide codopants. They found that Nd^{3+} , Dy^{3+} , Ho^{3+} , and Er^{3+} show similar behavior and noted a positive correlation between the trapping depth and the 4f-5d transition energy. These observations and the reported trapping depths of around 1 eV are fully consistent with Fig. 2, where indeed the ground state energies of Nd^{2+} , Dy^{2+} , Ho^{2+} , and Er^{2+} are similar and about 1 eV below the conduction band. The crucial difference is that Nakazawa and Machida and Yamamoto and Matsuzawa presume that the trivalent lanthanides are hole traps instead of electron traps, but their results can equally well be used in support of the electron-trapping model proposed in this work.

The scheme for SrAl_2O_4 also explains the observation by Hölsa^{27,31} and later by Ohta and Takami⁴³ that codoping of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ with Sm^{3+} or Yb^{2+} reduces the afterglow intensity drastically. Figure 2 shows that Sm^{3+} and Yb^{2+} form 2 and 2.7 eV deep electron traps. Such deep traps cannot be emptied at room temperature and therefore cannot contribute to persistent luminescence.

Recently the persistent luminescence properties of $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+};\text{Ho}^{3+}$ were reported by Guo *et al.*⁴⁴ The found activation energy for persistent luminescence of about 0.7 eV agrees well with the electron-trapping depth provided by Ho^{3+} in the scheme of Fig. 1. The suggestion by Guo *et al.* that Ho^{3+} traps a hole is not possible according to the level scheme. Valence band hole trapping is only possible when the Ho^{3+} ground state is located

above the top of the valence band, and in Fig. 1 it is located 2.45 eV below. The thermal quenching of Eu^{2+} 5d-4f emission should now be attributed to the thermal excitation of the 5d electron to the conduction band. The energy barrier of 0.2 eV for SrGa_2S_4 and 0.6 eV for CaGa_2S_4 agrees with Fig. 1.^{34,35}

Conclusions

The lack of a reliable method to determine the location of lanthanide impurity levels relative to the valence and conduction bands has led to various speculative models and mechanisms on persistent luminescence and Eu^{2+} luminescence quenching. Particularly the model involving the thermal release of a hole from Eu after it has been excited to its 5d state has been widely adopted since its first introduction by Matsuzawa *et al.*¹ The level schemes presented in this work are not consistent with this popular model. It is also not consistent with models to explain thermal quenching of Eu^{2+} emission by means of hole release. The schemes reveal that the mechanism should involve the ionization of the 5d electron to conduction band states. Dy^{3+} is then the electron trap and Eu^{2+} the hole trap. This view is fully consistent with many other observations and also explains why Sm^{3+} and Yb^{3+} codopants drastically reduce the persistence afterglow in aluminates and silicates.

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