Thiocyanates as Novel Host Lattices for Emitting Rare Earth Ions: Luminescence of $Sr(SCN)_2:Eu^{2+}$

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Excitation and emission spectra of $Sr(SCN)_2:Eu^{2+}$ at different temperatures are presented. A strong bright green emission due to $4f^65d^1 \rightarrow 4f^7$ transitions is observed at low temperature. The spectra of this new kind of host lattices are compared to those of sulfides and nitrides. This comparison shows that the influence of the degree of covalency of the host lattice is remarkably large. Additionally, some Fano antiresonances due to $^8S \rightarrow {}^6I_J$ and $^8S \rightarrow {}^6D_J$ transitions are observed in the excitation spectra. The luminescence is strongly quenched with increasing temperatures, and no emission could be observed above 220 K. The lifetime is 453 ns at 12 K. Due to the shape of the excitation spectra, the quenching behavior with increasing temperature, and the short lifetimes, it can be assumed that there is an increasing amount of nonradiative relaxation at higher temperature. These observations are explained by the fact that the excited $4f^65d^1$ state is located in the vicinity of the conduction band and the respective excitonic state is thermally populated followed by nonradiative relaxation to the ground state.

Introduction

Eu^{2+} ions possess exceptional luminescence properties which makes them interesting for several different applications. On one hand, the d → f emission is parity allowed and, thus, very intensive, while f → f transitions which are mainly observed for trivalent rare earth ions are parity forbidden. On the other hand, the energetic position of the excited d states depends very strongly on the host lattice, so that the energy of the emission varies with the cation's surrounding. While $BaMgAl_{10}O_{17}:Eu^{2+}$ shows a blue emission and is used as the blue phosphor in discharge lamps, $BaFBr:Eu^{2+}$ emits with a maximum at 389 nm and is used as a storage phosphor with applications in imaging plates for X-ray diffractometry and in medicine.[1] With an exact knowledge of the dependence of the luminescence on the crystal structure of the host lattice it would be possible to design luminescent materials with desired properties.

A schematic picture of the energetic diagram for the electronic states of a divalent rare earth ion is shown in Figure 1. The energetic position of the excited $4f^{n-1}5d^1$ states relative to the $4f^n$ ground state depends on the specific divalent ion and on the host lattice. When an ion is placed in a certain crystalline environment, the center of gravity is shifted to lower energy by an amount of ΔE_{cg} due to the wider spread of the electrons (Figure 1b). This is called the nephelauxetic effect. In this case, the amount of covalency is the main factor of influence. The degree of covalency is mainly determined by the ligands. But also the second coordination sphere which polarizes the bonds to a different amount is of some importance. This is illustrated by the remarkable difference of 400 cm^{-1} in the emission maxima of the isotypic compounds $SrCdCl_4:Eu^{2+}$ and $SrZnCl_4:Eu^{2+}$.[2] Additionally, in a crystal field which is described by the microscopic point symmetry, the five 5d states are split in a well-known manner which is described by ligand field theory (Figure 1c). While for transition metals emission due to transitions between the different d crystal field levels can be found in some cases, the emission of divalent rare earth ions is due to transitions of the lowest 5d level to the $4f^n$ ground state if no excited 4f states are involved. Therefore, the shift of the center of gravity of the 5d states in the spherical symmetrical field will show an effect on the emission energy. It can be assumed that the difference of

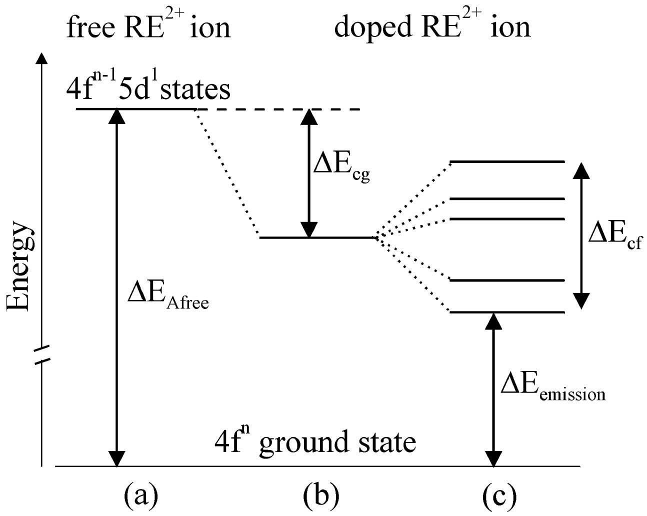

Figure 1. Schematic picture of the influence of the environment of a divalent rare earth ion on the positions of the electronic states (see text).

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the shift is large for different kind of anions but respective investigations are scarce. While in the past mainly oxides were used as host lattices resulting mostly in an ultraviolet or blue emission of Eu^{2+}, there are only a few studies on the luminescence of Eu^{2+} in halides, sulfides, and selenides.[3−6] There are nearly no investigations on the influence of nitride ions.[7,8] In the case of sulfur or nitrogen coordination spheres the increased covalency shifts the center of gravity and, therefore, shifts the lowest excited 5d state to lower energy, leading to a green or red emission. Moreover, phosphors which emit in the low energy range are of considerable interest for bright LEDs based on the UV emission of GaN, which are developed by lamp industries at present.

Due to the reasons described above thiocyanates should be a very interesting new type of host lattice with a sulfur and/or nitrogen coordination sphere which is less covalent compared to sulfides and nitrides. This forced us to synthesize the alkaline earth thiocyanates M(SCN)$_2$ (M = Ca, Sr, Ba)[9,10] and to solve their crystal structures. The alkaline earth thiocyanates are suitable host lattices for divalent rare earth ions because phase pure samples are easily available by dehydration of the respective hydrates. Moreover, Eu(SCN)$_2$ crystallizes with the same crystal structure in the form of lemon-colored transparent cubes with a size up to (2 × 2 × 2) mm^3.[10] In the case of M = Sr, Ba, Eu the compounds melt without decomposition so that doping can be achieved by melting the alkaline earth compounds together with a small amount of Eu(SCN)$_2$. Furthermore, the radius of Sr^{2+} is similar to that of Eu^{2+}, so that doping will cause no distortion of the host lattice which is of importance for the investigation of the influence of the surrounding on the luminescence.

In the present paper the luminescence of a divalent rare earth ion doped in a thiocyanate host lattice namely, Sr(SCN)$_2$:Eu^{2+}, is presented. The results are compared to those of Eu^{2+} doped sulfides and nitrides to elucidate the influence of the degree of covalency for host lattices with the same kind of atoms in the coordination sphere.

Crystal Structure of Sr(SCN)$_2$. The crystal structure of Sr(SCN)$_2$ is already described.[10] It crystallizes with the space group *C*2/*c*. Crystallographically there is one distinct Sr^{2+} ion which occupies the site 4e with point symmetry C$_2$. The structure contains alternating layers of Sr^{2+} and SCN$^-$ ions, respectively. According to the formulation Sr(SCN)$_{4/4}$(NCS)$_{4/4}$ Sr^{2+} is 8-fold coordinated by four nitrogen and four sulfur atoms forming a square antiprism (Figure 2). The distances Sr−N (2 × 268.8 pm, 2 × 271.5 pm) and Sr−S (2 × 311.3 pm, 2 × 316.6 pm) are almost identical to those in Eu(SCN)$_2$,[10] so that doping can be achieved without distortion of the lattice.

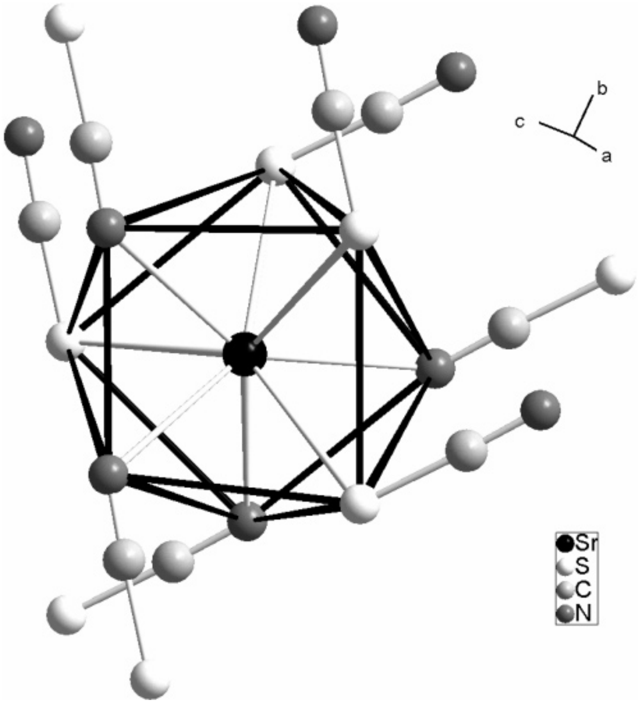

Figure 2. Representation of the[Sr(SCN)$_8$]-polyhedra in Sr(SCN)$_2$. The coordination polyhedron is drawn as black lines.

Experimental Section

Phase pure samples of Sr(SCN)$_2$ were obtained by dehydration of Sr(SCN)$_2$·3H$_2$O at 150 °C in dynamic vacuum. Samples of Eu(SCN)$_2$ were prepared by the metathesis reaction of NaSCN (Merck, 98.5%) and EuCl$_2$.[10] To avoid contamination with oxygen, which is frequently included in commercial samples, EuCl$_3$ was synthesized via the ammonium halide route from Eu$_2$O$_3$ (Johnson-Matthey, 99.9%)[11] and reduced to EuCl$_2$ at 500 °C in an H$_2$/Ar stream. Phase pure samples of Eu(SCN)$_2$ were easily obtained by manual separation of the yellow crystals of Eu(SCN)$_2$ from the reaction mixture. The phase purity of Eu(SCN)$_2$ and Sr(SCN)$_2$ was checked by powder X-ray diffraction methods (Stoe and Cie, Stadi P). Samples of Sr(SCN)$_2$:Eu^{2+} (0.05%) were obtained by melting of the thiocyanates in the appropriate molar ratio in silica ampules. The melting point of Sr(SCN)$_2$ was determined to be 348 °C while the decomposition starts at 650 °C.[10] Therefore, the reaction mixture was heated to 360 °C followed by slow (1 °C/h) cooling using the Bridgman technique.

Photoluminescence emission and absorption spectra were recorded using a spectrofluorometer (SPEX, DM3000F) equipped with two 0.22-m double monochromators (SPEX, 1680) and a 450 W xenon lamp. Cooling down to 4.2 K was achieved with a liquid helium flow cryostat (Oxford, LF 205). The emission spectra were corrected for photomultiplier sensitivity, the excitation spectra were corrected for lamp intensity, and both were corrected for the transmission of the monochromators.

Temperature-dependent decay measurements were performed using a frequency tripled Nd:YAG laser (Spectra Physics, GCR 11, 355 nm) as excitation source with a pulse length of 8 ns and an energy of 5 mJ/pulse. The detection system included a 0.27-m single monochromator (Spectroscopy Instruments) and a photon counting system (Stanford, SR400). Measurements at specific low temperatures down to 12 K were performed with the help of a closed-cycle helium cryostat (Air Products).

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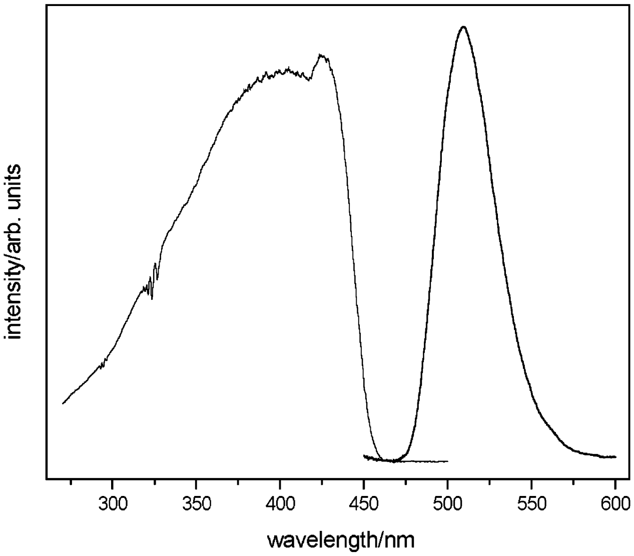

Figure 3. Excitation (left) and emission (right) spectra of $Sr(SCN)_2$:Eu^{2+} at 4.2 K.

Results and Discussion

Luminescence at Low Temperature. $Sr(SCN)_2$:Eu^{2+} shows a strong bright green luminescence at low temperature. The respective emission spectrum at 4.2 K excited at 428 nm is depicted in Figure 3. A broad band is detected with a maximum at 508 nm (19685 cm^{-1}) and full width at half maximum $\Gamma = 1548$ cm^{-1}. This band can be assigned to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Because exclusively one transition is observed, all Eu^{2+} ions occupy identical sites. This is expected because there is only one crystallographically distinct Sr^{2+} ion in $Sr(SCN)_2$.[10] The shape of the band is nearly symmetrical on an energy scale with a slightly steeper drop on the high energy side. For a large change of the metal ligand distance in the ground and the excited state, Δr, the emission band should be completely Gaussian shaped. Therefore, in the present case Δr and, thus, the Stokes shift and the Huang–Rhys factor should not be extremely large.

The excitation spectrum at 4.2 K detected at an emission wavelength of 510 nm is also shown in Figure 3. A very broad nearly unstructured band is observed due to transitions to the $4f^65d^1$ states. These are split to five single levels because of the C_2 point symmetry of the cationic site. The onset of the excitation band is at 462 nm (21645 cm^{-1}) and the first excitation maximum is at 426 nm (23474 cm^{-1}). The Stokes shift determined by the maxima of the emission and excitation bands is 3789 cm^{-1}. Transition to single ^7F_J states of the $4f^65d^1$ levels are not resolved in the present case. This shows that the exchange interaction between the six 4f electrons and the 5d electron is large[12] as expected for a thiocyanate host lattice. On the other hand, the observation of the $4f^6(^7F_0)5d^1$ state in the excitation spectrum is necessary for an accurate determination of the Stokes shift because the emission originates exclusively from the $4f^6(^7F_0)5d^1$ state. For the halide borate host lattices $M_2B_5O_9X$ (M = Ca, Sr, Ba; X = Cl, Br) doped with Eu^{2+} ions an observation of the $4f^6(^7F_0)5d^1$ states and, therefore, an exact determination of the Stokes shifts, was possible.[13] These results show that the values of the Stokes shift considering the $4f^6(^7F_0)5d^1$ states are in general much smaller than those determined by the two maxima. Thus, the above-mentioned value of 3789 cm^{-1} is only an upper limit for the Stokes shift—the real value may be much lower. According to Dorenbos,[3] for a better estimation of the Stokes shift the energetic position of the $4f^6(^7F_0)5d^1$ state is taken where the excitation energy decreases to 20% on the long wavelength side of the first maximum. This leads to 450 nm (22220 cm^{-1}) for the first excitation transition and to about 2535 cm^{-1} for the Stokes shift.

It is interesting to compare the results to those of Eu^{2+} doped nitrides and sulfides. Dorenbos[4] listed the respective values for different host lattices known so far, and for simplicity I adopt his names of the parameters. In this work, the energy of the excitation to the lowest 5d state for a given host lattice is expressed as difference ($D(2+, A)$) from that of the free gaseous Eu^{2+} ion which is at $E_{\mathrm{Afree}}(7,2+) = 34000$ cm^{-1},[4] e.g.

$$E_{\mathrm{abs}}(7, 2+, A) = E_{\mathrm{Afree}}(7,2+) - D(2+, A)$$

A is a parameter which describes the effect of the host lattice. The energy of the emission band is described by further subtraction of the Stokes shift $\Delta S(2+, A)$

$$E_{\mathrm{em}}(7, 2+, A) = E_{\mathrm{Afree}}(7,2+) - D(2+, A) - \Delta S(2+, A)$$

In the case of $Sr(SCN)_2$:Eu^{2+} $D(2+, A)$ equals 11780 cm^{-1} and the estimated Stokes shift is 2535 cm^{-1} as described above.

There are some studies of the luminescence of Eu^{2+} doped in sulfides.[4] Most of the host lattices are ternary compounds $M_xA_yS_z$ (M = alkaline earth ion, A = Al, Ga). Because Ba^{2+} cations cause a smaller crystal field splitting of the 5d states than Sr^{2+} cations it is much more convenient to take host lattices containing the latter for comparison. In this case, the red shift is always larger; on average the difference is about 2000 cm^{-1}. The Stokes shift is smaller in all these cases.

Binary compounds are much more suitable for comparison because in ternary compounds the second cation polarizes the S^{2-} anions resulting in an increasing ionicity of the Eu–S bond. Therefore, a comparison with the binary sulfides, above all SrS, is most gainful. The red shift for SrS:Eu^{2+} is $D(2+, A) = 15\,706$ cm^{-1},[14] this is a difference of 4000 cm^{-1} compared to the thiocyanate. This shows that the influence of covalency is very large! The Stokes shift of SrS:Eu^{2+}, $\Delta S(2+, A) = 2223$ cm^{-1}, is comparable to that of $Sr(SCN)_2$:Eu^{2+}. However, the alkaline earth sulfides adopt the NaCl type structure, which means that the cations are octahedrally coordinated by S^{2-} anions in contrast to the 8-fold coordination in the case of the thiocyanates. Thus, the two host lattices are not very comparable. On the other hand, the red shift is a sum of the shift of the center of gravity of the 5d states and the splitting caused by the crystal field. Because of the large covalency and the long cation–sulfur distances the

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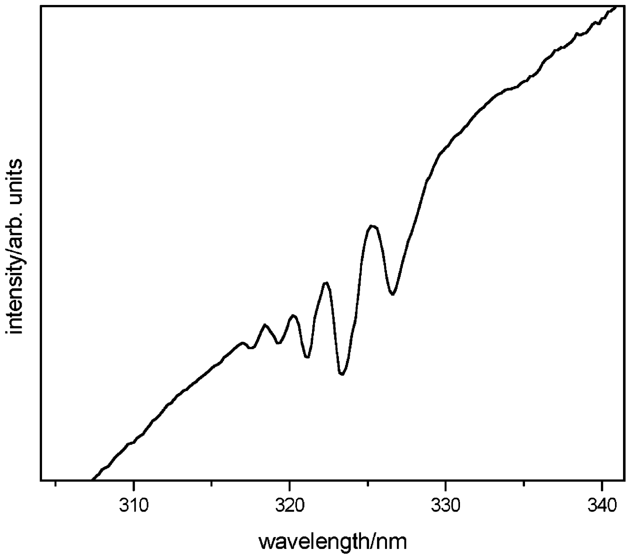

Figure 4. Part of the excitation spectrum of $Sr(SCN)_2$:Eu^{2+} at 4.2 K in the region of the $^8S \rightarrow {}^6I_J$ transitions.

centroid shift is much larger than the splitting in the case of a sulfur coordination, so that it is reasonable to compare both host lattices.

Because of the lack of data it is much more difficult to compare the results of the thiocyanate to nitridic host lattices.[4] There are only three barium compounds and one calcium compound which can be taken for comparison.[7,8] All of these are ternary compounds. Interestingly, there is no influence of the size of the cations in these host lattices because the red shifts are very comparable in these cases. All investigated nitrides luminesce in the red or orange region. This means that the red shift is at least 4000 cm^{-1} larger for the nitrides compared to $Sr(SCN)_2$:Eu^{2+}, whereas the Stokes shifts are, again, smaller or comparable. It can be assumed that the differences of the red shifts should be much larger in comparison with the binary nitrides, although the crystal structures of M_3N_2 are not known for M = Sr, Ba (maybe due to its difficult preparation). Comparison to nitridic host lattices shows again the large influence of the covalency to the emission energy of Eu^{2+} ions!

In the excitation spectrum the intensity decreases nearly linearly with increasing energy (Figure 3). This shape of the excitation spectrum cannot be explained by decreasing intensity of the excitation lamp because the spectrum is corrected for the lamp intensity. On the other hand this behavior at higher excitation energies may be due to photoionization followed by nonradiative return to the ground state (see below). Another explanation of this observation is host lattice absorption if the probability of energy transfer to the luminescent ion is low.

Some dips located around 320 and 295 nm are observable in the excitation spectrum (Figure 4). The energetic positions of these dips are listed in Table 1. They coincide with the energy of the $^8S \rightarrow {}^6I_J$ and $^8S \rightarrow {}^6D_J$ transitions within the $4f^7$ electronic configuration of Eu^{2+}. Fano and Copper[15] described a theoretical explanation for a band profile of a broad continuum in the vicinity of sharp peaks. Therefore, this phenomenon is called Fano antiresonance. It can be applied to the resonance of sharp parity-forbidden f−f transitions and broad 4f−5d bands. Because the positions of the 4f ↔ 4f transitions are nearly independent of the host lattice they are at energy comparable to that of Eu^{2+} in other compounds and can be assigned undoubtedly. Fano antiresonances of the respective transitions were already studied by Meijerink and Blasse.[16] Note that no $^8S \rightarrow {}^6P_J$ transitions are observed in the present work or in ref 16. These are detected by two photon spectroscopy and are located around 360 nm.[17] Besides, $^6P_{7/2} \rightarrow {}^8S$ emission is observed if the 5d bands are located at higher energy. This is the case for example in $KMgF_3$:Eu^{2+} where $^6I_{7/2} \rightarrow {}^8S$ transitions also could be detected.[18] The lack of the antiresonances due to the ^6P_J states can be explained by the weak coupling of these states with the $4f^65d^1$ state.[16,17] The errors of an analysis of the exact positions of the f−f transitions are rather large due to the uncertainty of the shape of the $4f^65d^1$ band. For this reason, no analysis was carried out in this work. Furthermore, the large number of Stark components which are situated very close in energy[17] makes an assignment of the transitions impossible. A comparison of the energies of the detected Fano antiresonances in $Sr(SCN)_2$:Eu^{2+} to those in SrB_5O_9Br:Eu^{2+} and $BaSiO_4Br_6$:Eu^{2+}[16] shows a shift to lower energy by about 100 cm^{-1}. This can be explained by the increased covalency of the thiocyanate which causes a different spin−orbit and crystal field splitting.

Table 1. Positions of the Fano Antiresonances in $Sr(SCN)_2$:Eu^{2+}

level	λ/nm	E/cm^{-1}
^6I_J	326.6	30618
^6I_J	323.4	30921
^6I_J	321.2	31133
^6I_J	319.4	31309
^6I_J	317.6	31486
^6D_J	296.2	33761
^6D_J	294.4	33967
^6D_J	292.8	34153

Temperature-Dependent Emission and Lifetimes. The emission of $Sr(SCN)_2$:Eu^{2+} is strongly quenched with increasing temperatures and not observable at room temperature. The emission intensity dependence on the temperature using an excitation energy of 428 nm is depicted in Figure 5. The temperature at which the intensity is half of that at 4.2 K is $T_{1/2}$ = 157 K, and at 220 K the emission is completely quenched.

Lifetime measurements excited at 355 nm were performed between 12 and 155 K. All decay curves are single exponential. The respective decay times are also shown in Figure 5. Above 155 K (τ = 13 ns) no lifetime measurements could be performed due to our experimental equipment. At 12 K the decay time is 453 ns, while the decay time is half of its maximum value at $T_{1/2}$ = 75 K. The difference between the decrease of the intensity of the emission and that of the lifetime in relation with temperature is remarkable. This might be due to several reasons. First, the excitation energy used for the lifetime measurements (355 nm) is much higher

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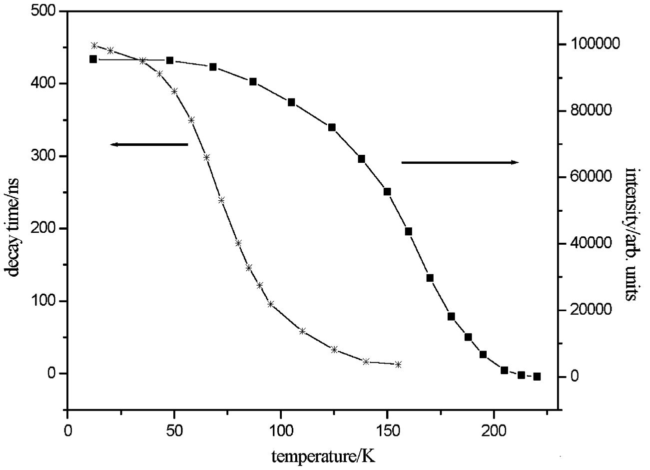

Figure 5. Temperature dependence of the integrated emission intensity (■) and decay time (*) of $Sr(SCN)_2:Eu^{2+}$.

than those for the emission intensity (428 nm). An excitation energy of 355 nm might be suitable to excite the electron into or close to the conduction band which would decrease the lifetimes due to nonradiative excitonic decay (see below). Additionally, the sample will be heated due to irradiation of the high-power Nd:YAG laser beam, so the measurement of the temperature may be not correct. Furthermore, the absorption of the excitation radiation varies with temperature due to broadening of the excitation band with increasing temperature. This alteration is different for different excitation energies, which can be expect to be the major reason for the observed difference.

The lifetimes of $Sr(SCN)_2:Eu^{2+}$ exhibit rather small values compared to these found for Eu^{2+} doped in other host lattices.[19] A simplified relation between the transition probability per unit time and the radial integral $\langle 5d|r|4f\rangle$ is given by[19]

$$A_{\mathrm{tot}}\,(\mathrm{Eu}) = 1/\tau = 5.06 \times 10^{-8}\ |\langle 5d|r|4f\rangle|^2\ \chi\sigma^3$$

where σ is the wavenumber of the emitted light in units of cm^{-1}, and χ is a term which expresses the dependence on the index of refraction of the host lattice n

$$\chi \approx n\,(n^2 + 2)^2/9$$

Because the index of refraction is not known for $Sr(SCN)_2$ a value of $n = 1.65$ was estimated based on the known indices of other thiocyanates.[20] This yields $\langle 5d|r|4f\rangle = 1.18$ Å. The estimated value for the radial integral is very large compared to the respective values for oxides,[19] where the largest value is 0.92 Å. Even if one would take a larger value 1.8 for n, the integral would be equal to 1.02 Å. This would mean that the delocalization of the excited state is much smaller for $Sr(SCN)_2:Eu^{2+}$ than in oxidic host lattices. In fact, this cannot be true. The short decay time is responsible for the large radial integral. This points to a reduction of the lifetime due to nonradiative processes.

As an explanation for the short lifetime, multiphonon 5d → 4f relaxation may serve. Due to the values of the highest-energy phonons found for the thiocyanates ($Eu(SCN)_2$, $h\nu_{\max} = 2064$ cm^{-1}; $Sr(SCN)_2$, $h\nu_{\max} = 2065$ cm^{-1} [10]) compared to those of the emission energy it can be assumed that this process is of rather low probability in the present case.

The luminescence behavior of $Sr(SCN)_2:Eu^{2+}$ can be better explained by photoionization of the excited states in the conduction band of the host lattice. Moine and Pedrini[21,22] reported some interesting studies on the luminescence of $BaF_2:Eu^{2+}$. They found an emission with a large red shift which was ascribed to an impurity trapped exciton because the excited states are localized in the conduction band. The same behavior was described by McClure and Pedrini for $SrF_2:Yb^{2+}$.[23] In $BaGa_2O_4:Eu^{2+}$ no luminescence was observed even at low temperature.[24] This behavior was explained by the assumption that again the excited states lie in the conduction band and the exciton recombines nonradiatively. In fact, several cases are known where the host lattices induce an "anomalous" luminescence of Eu^{2+} and Yb^{2+}[5] at the present. In the case of $Sr(SCN)_2:Eu^{2+}$ the observations can be interpreted similarly. The bottom of the excited state may be located near the bottom of the conduction band. After excitation, conventional d → f emission or nonradiative exciton relaxation due to thermal population of the excitonic state may occur. At increasing temperature, the population of the excitonic state increases and the radiative emission intensity decreases. The excitonic relaxation must be nonradiative because only one single emission band is observed even at higher temperature. Additionally, if emission spectra are taken at higher excitation energy (320 nm) a similar band as shown in Figure 3 is detected but with a lower emission intensity. Another fact which supports the given explanation is the extremly short lifetime even at 12 K and the decreasing intensity in the excitation spectrum with increasing energy. It can be assumed that the states at higher excitation energies are located in the conduction band. After high energy excitation photoionization or direct band excitation may occur and no emission can be observed. Another possibility is relaxation to the lowest excited state followed by conventional emission. These two processes will compete, and the emission intensity will decrease. A similar situation is described for $CaSO_4:Yb^{2+}$[25] even if the decay times are much longer due to the lower probability of the Yb^{2+} emission.

On the other hand, the observed Stokes shift (2535 cm^{-1} = 0.31 eV) shows that the emission is due to "normal" d → f transition. For d → f emission values of 0.1 to 0.5 eV are observed, while those for exciton emission are much larger.[5] Additionally, in $Ba(SCN)_2:Eu^{2+}$ the excitation band is shifted to slightly higher energy as it is expected due to the lower splitting of the 5d states; the emission band is slowly red shifted compared to the strontium compound[26] (caused by the larger increase of the metal ligand distance during

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excitation) while the quenching temperature is much higher ($T_{1/2} = 181$ K). This behavior can be explained by the assumption of a similar situation, but with a larger distance of the lowest 5d state to the conduction band.

Conclusions

The luminescence properties of Eu^{2+} doped in $Sr(SCN)_2$ are presented. A bright green emission at a maximum of 508 nm is observed at low temperature, which is quenched at increasing temperature and not observable above 220 K. The Stokes shift is about 2535 cm^{-1}. Comparison to sulfides and nitrides shows that the influence of the covalency of the host lattice on the position of the excited $4f^65d^1$ states is large. Some Fano antiresonances due to $^8S \rightarrow {}^6I_J$ and $^8S \rightarrow {}^6D_J$ transitions are observed in the excitation spectra. The lifetime of the emission is rather short compared to that of other Eu^{2+} doped compounds. An estimation of the radial integral from the decay time shows that there must be a channel of nonradiative decay. Furthermore, the intensity of the excitation spectrum decreases with increasing energies. This can be explained by the fact that the lowest excited state is located closely below the conduction band. After excitation the excitonic state is thermally populated from the $4f^65d^1$ state followed by nonradiative excitonic *and* radiative d → f emission.

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