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Valence Stability of Lanthanide Ions in Inorganic Compounds

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New methods are available to position the energy levels of divalent lanthanide impurities in wide band gap inorganic compounds (halides, chalcogenides) relative to the conduction and valence bands. These methods are used to determine the energy difference (E_{Ff}) between the $4f^n$ ground state of the lanthanide and the Fermi energy assumed to be located midway between the top of the filled valence band and the bottom of the empty conduction band. It is demonstrated that E_{Ff} provides a measure for the stability of the divalent lanthanide against oxidation to the trivalent state and the stability of the trivalent one against reduction. The relation between E_{Ff} and the lanthanide valence state and how E_{Ff} depends on type of lanthanide ion and type of inorganic compound is addressed.

Introduction

Eu^{2+}, Yb^{2+}, Sm^{2+}, and Tm^{2+} are the most studied divalent lanthanides in solids of which Sm^{2+} and Tm^{2+} are the most difficult to stabilize. In oxide compounds a reducing agent (H_2−N_2 or H_2 atmosphere, carbon or CO, or rare earth metal vapor) is required to stabilize the divalent state, but in some oxides Eu^{2+} and Yb^{2+} and to lesser extent also Sm^{2+} and Tm^{2+} can be obtained even under oxidizing conditions. A study of this phenomenon was pioneered by Su et al.[1] They showed that Eu in SrB_4O_7,[2] SrB_6O_{10},[3] BaB_8O_{13},[1] $Sr_4Al_{14}O_{25}$,[4] and $BaMgSiO_4$[5] can be obtained in the divalent state by synthesis in air at high temperature.

The valence stability and valence change has attracted attention from an applied physics point of view,[6−9] but there is also fundamental interest. However, models to predict these properties are not available yet. In this work, the valence stability of lanthanides is related to the location of the lanthanide ground-state energy relative to the Fermi energy in the un-doped inorganic compound. This latter energy is assumed located midway between the top of the valence band and the bottom of the conduction band. Recently developed methods are used to position the lanthanide ground state relative to this Fermi energy. Finally, relationships between valence stability and absolute level energies are demonstrated.

The paper does not aim to provide an in depth explanation of valence stability of lanthanide ions in one specific compound. The aim is to provide an overview that covers many different types of compounds (fluorides, chlorides, oxides, sulfides). A phenomenological approach was chosen to identify the main trends regarding the changing stability with parameters like the type of anions in the compound, the site size, and the band gap of the compound. It is expected that knowledge of these trends and their relationship with the location of the lanthanide energy levels relative to the host levels will initiate more refined studies.

Results and Discussion

The energy (E^{CT}) needed to transfer an electron from the valence band of an inorganic wide band gap compound to a trivalent lanthanide impurity provides information on the location of the ground state of the corresponding divalent lanthanide ion.[10,11] This statement has been known for a long time, but until recently it was not utilized to systematically determine energy level locations of divalent lanthanide ions. From an analysis of the literature on Eu^{3+} luminescence and its excitation, the energy (E^{CT}) of charge transfer to Eu^{3+} in a wide collection of compounds (fluorides, chlorides, bromides, oxides, sulfides) was derived. For the same collection of compounds also information on the energy needed to excite the host lattice (i.e., the energy, E^{ex}, to create a bound electron−hole pair (exciton)) was gathered. The data on E^{CT} and E^{ex} together with all the references can be found in ref 12.

As demonstration of how to use E^{ex} and E^{CT}, Figure 1 shows the energy level scheme of $CaGa_2S_4$. The top of the fully occupied valence band is defined as zero energy. The bottom of the empty conduction band is at energy (E_{VC}). As a rule of thumb we will assume that $E_{VC} = 1.08E^{ex} \approx 4.9$ eV (i.e., the binding energy of the electron−hole pair in the exciton is about 8% of the exciton creation energy). A

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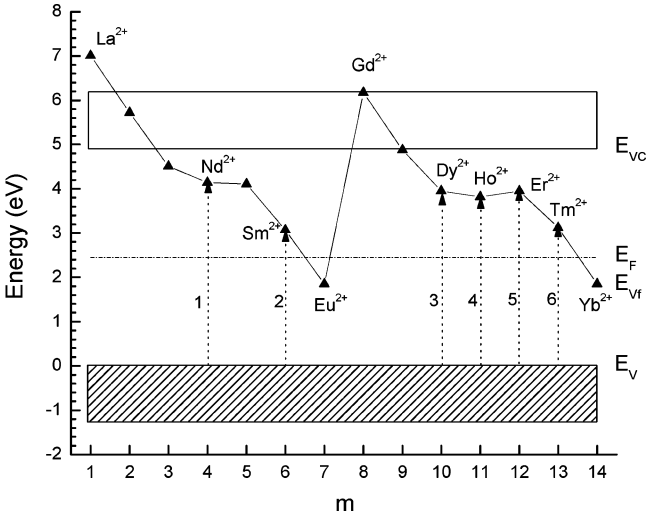

Figure 1. Position of the lowest 4f state of divalent lanthanide ions in $CaGa_2S_4$. *m* is the number of electrons in the $4f^m$ configuration of the divalent lanthanide ion.

motivation can be found in ref 12. Midway between the bottom of the conduction band and the top of the valence band, the Fermi energy level (E_F) is drawn. When we assume that the Fermi level does not change much when compounds are doped with small (say <0.3 mol %) concentrations of lanthanide impurities, then at thermal equilibrium and at low-temperature levels below E_F should be occupied and levels above should be unoccupied.

The length of the arrows numbered 1 through 6 indicate experimentally observed energies of charge transfer from S^{2-} to Nd^{3+} (arrow 1), Sm^{3+} (arrow 2), Dy^{3+} (arrow 3), Ho^{3+} (arrow 4), Er^{3+} (arrow 5), and Tm^{3+} (arrow 6).[13] Experimental data indicate that they start at the top of the valence band and end at the ground state of the corresponding divalent lanthanide ion.[11] On the basis of many observations covering many different compounds, a universal behavior was found that can be used to draw the ground states for all divalent lanthanides when that of only one of them (usually Eu^{2+}) is known.[11] In Figure 1, these ground-state energies are connected by the curve denoted as E_{Vf}. The universal curve has a minimum when the 4f shell is half-filled ($m = 7$ for Eu^{2+}), completely filled ($m = 14$ for Yb^{2+}), and maxima when $m = 1$ (La^{2+}) and $m = 8$ (Gd^{2+}). It reflects the strength of electron binding within the 4f shell as described by the Jörgensens spin-pairing theory.[14]

In this work, the information presented in ref 12 is used to determine the energy difference ($E_{Ff} \equiv E^{CT} - 0.54E^{ex}$) between the electron in the Eu^{2+} ground state and the Fermi energy. It will be demonstrated that this energy difference is an important parameter that determines the preferred valence of Eu in compounds. Theoretically, Eu should prefer the divalent state when $E_{Ff} < 0$ and the trivalent state when $E_{Ff} > 0$. This situation is further illustrated in Figure 2a where level 1 below E_F is occupied, denoting that the lanthanide is in the divalent state, and level 2 is unoccupied, denoting that it is in the trivalent state. The situation for Eu^{2+} is easily generalized to the other divalent lanthanides. The level scheme for $CaGa_2S_4$ shows, for example, that $E_{Ff} < 0$ for Eu and Yb and that these lanthanides should enter the compound in the divalent state while all other lanthanides have $E_{Ff} > 0$ and prefer the trivalent state. This is precisely what is observed experimentally.[15,16]

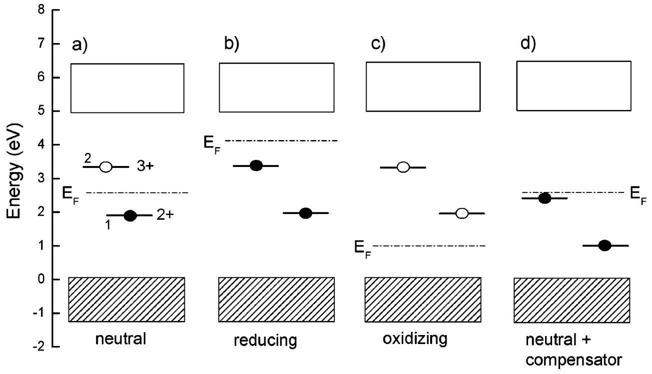

Figure 2. Influence of synthesis conditions on the Fermi energy (E_F) and related reduction and oxidation properties. (a) is in a neutral atmosphere. Level 1 is occupied (the divalent state), and level 2 is un-occupied (the trivalent state). (b) is in a reducing atmosphere. (c) is in an oxidizing atmosphere. (d) shows the influence of a charge-compensating ion on the level energies in a neutral atmosphere.

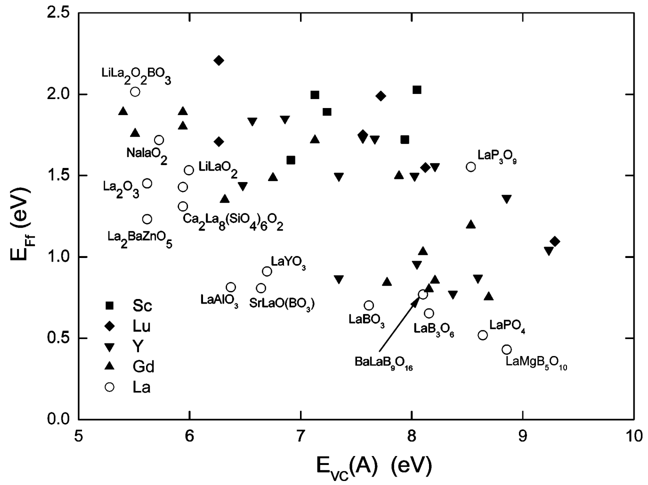

Figure 3. E_{Ff} for Eu^{2+} on La, Gd, Y, Lu, and Sc sites in rare earth based oxide compounds against the band gap of the material.

Figure 3 shows the values for E_{Ff} of Eu located on either a La^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}, or Sc^{3+} site in oxide compounds. Only the data on the La-based compounds are labeled with the names in Figure 3. The trivalent rare earth compounds were selected because of the many data available on these materials, which enables us to study trends in E_{Ff}. Three clear trends are observed: (1) E_{Ff} is always positive. (2) E_{Ff} tends to increase with smaller size of the occupied rare earth site (i.e., in the sequence La, Gd, Y, Lu, and Sc). (3) E_{Ff} decreases when the band gap increases. Figure 3 shows clearly that, apart from LaP_3O_9, the La-based compounds have the smallest E_{Ff} that decreases with larger band gap. Why LaP_3O_9 deviates from the general trends is not clear; it may indicate that that data is wrong. Because E_{Ff} is always positive, the

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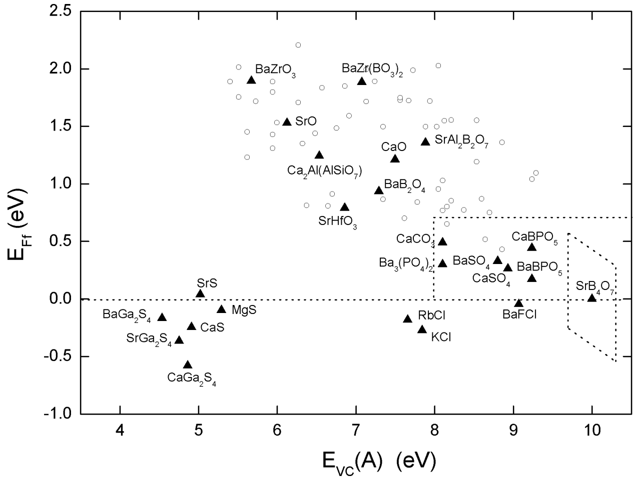

Figure 4. E_{Ff} for Eu^{2+} in oxide, chloride, and sulfide compounds. The solid triangle symbols pertain to Eu on Ba^{2+}, Sr^{2+}, Ca^{2+}, or Mg^{2+} sites and in addition to Eu in RbCl and KCl. The other data are the same data as in Figure 3 and pertain to Eu in trivalent rare earth oxide compounds. The box around data with $E_{VC} > 8$ eV and $E_{Ff} < 0.7$ eV contains alkaline earth compounds in which Eu^{2+} can be obtained even under oxidizing conditions.

trivalent state of Eu is the preferred one on trivalent rare earth sites in oxide compounds. Indeed there are very few reports about Eu^{2+} on trivalent rare earth sites in oxide compounds even when prepared under reducing conditions.[17]

The situation can also be analyzed for Eu on divalent Ca, Sr, or Ba sites in oxide compounds. Figure 4 shows the values for E_{Ff} in these compounds. Like in Figure 3, E_{Ff} is positive indicating that the trivalent state is preferred even on the divalent cation sites. Nevertheless in most of these compounds divalent Eu can be introduced without difficulty when the compound is synthesized in a reducing atmosphere.

For some Ca-, Sr-, and Ba-based compounds, it is possible to obtain Eu^{2+} even when the compound is prepared under oxidizing conditions at high temperature. Well-known examples are SrB_4O_7, SrB_6O_{10}, and $Ba_3(PO_4)_2$ where Eu^{3+}, Yb^{3+}, and even Sm^{3+} and Tm^{3+} can be reduced to the divalent state by heating in air.[1] Eu can also be reduced to the divalent state in BaB_8O_{13}, but less Eu^{2+} is obtained than for SrB_4O_7.[18] Also MSO_4 and $MBPO_5$ (M = Ca, Sr, Ba),[19] $BaMgSiO_4$,[5] $Sr_3(PO_4)_2$,[20] and $Sr_2B_5O_9Cl$ are known to show reduction in air atmosphere. $Sr_4Al_{14}O_{25}$ was the first aluminate compound found to show this phenomenon.[4] On the other hand in $Sr_3(BO_3)_2$ and $Sr_2B_2O_5$, Eu cannot be reduced to Eu^{2+} in air.[3]

Various explanations were given for these reduction phenomena. Pei et al.[2,21] and Machida et al.[22] suggested a relationship with the existence of BO_4 groups in the borate network. The rigid tetrahedron structure of anions prevents the attack of oxygen from air on Eu during synthesis.[3] A relation with presence of tetrahedrons was also suggested for compounds with tetrahedral phosphate, silicate, and aluminate groups.[1] Indeed Eu^{3+} can be reduced to Eu^{2+} in $M_3(PO_4)_2$ (M = Sr, Ba)[20,23] and $MBPO_5$ (M = Ca, Sr, Ba).[1,18,24]

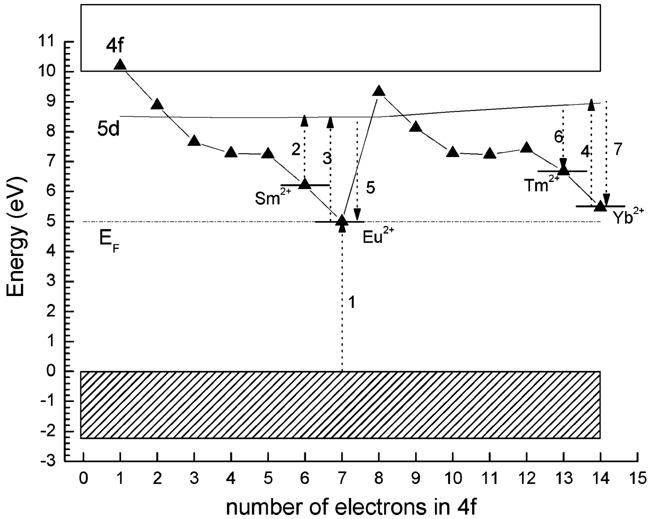

Figure 5. Energy level position of the lowest 4f and lowest 5d state of divalent lanthanide ions in SrB_4O_7.

SrB_4O_7 deserves special attention. Besides a unique stabilization of Eu^{2+}, this compound also shows a unique stabilization of Sm^{2+}.[25] The excitation spectrum of Eu^{3+} emission in SrB_4O_7 reveals that the fundamental absorption of the host lattice starts around 140−150 nm (8.3−8.9 eV).[26] The excitation spectra of Pr^{3+} and Ce^{3+} luminescence have a common feature. They both reveal a sharp drop in efficiency near 10 eV.[27,28] This drop can be attributed to the creation of free electrons in the conduction band and free holes in the valence band. The bottom of the conduction band in SrB_4O_7 is therefore estimated at 10 ± 0.3 eV, which is very large for an oxide compound. These values are used in Figure 5 to draw the bottom of the conduction band and the Fermi energy. The energy needed for charge transfer from the valence band to Eu^{3+} is also not yet well-established. Values of 5.4, 4.9, and 4.5 eV were reported.[26,29,30] Differences may arise from different charge compensating defects. Arrow 1 in Figure 5 shows the charge transfer to Eu^{3+} assuming about 5.0 eV energy. Arrows 2−4 show the observed transitions to the first 5d state of Sm^{2+}, Eu^{2+}, and Yb^{2+}; arrows 5−7 show the observed emissions in Eu^{2+}, Tm^{2+}, and Yb^{2+}.[31] The information on charge-transfer energy and energy differences between 4f and 5d is sufficient to construct the first 4f and 5d levels for all 14 lanthanides in the scheme of Figure 5.[11]

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With the now known values for E_{Ff} in Figure 4 and schemes such as Figure 1 and Figure 5, we may interpret the ability to reduce lanthanides to the divalent state with a quantitative approach (i.e., the magnitude of E_{Ff} controls the valence stability). E_{Ff} values are known for $CaSO_4$, $BaSO_4$, SrB_4O_7, $BaBPO_5$, $CaBPO_5$, and $Ba_3(PO_4)_2$ (see Figure 4). The data on all these compounds are found within the borders E_{Ff} < 0.7 eV and E_{VC} > 8 eV, suggesting a correlation between the ease of reduction and a small value for E_{Ff}. These borders are shown with dashed lines in Figure 4. The uncertainties in the location of the bottom of the conduction band and the value for E^{CT} in SrB_4O_7 results in errors in E_{Ff}. The skewed box drawn around the data symbols for SrB_4O_7 indicates the possible range of E_{Ff} and E_{VC} values. Further dedicated studies are required to obtain more accurate values.

The observed trend that E_{Ff} decreases with increasing value for the band gap can be applied to the Sr−borate sequence $Sr_3(BO_3)_2$, $Sr_2B_2O_5$, SrB_2O_4, SrB_4O_7, and SrB_6O_{10} of compounds. In that order, the boron content increases leading to increasingly stronger binding of the oxygen ligands in the borate networks. Although, accurate data on the band gaps are not available, it is expected that the band gap tends to increase and E_{Ff} to decrease in that sequence. The observation that Eu cannot be reduced in air to Eu^{2+} in $Sr_3(BO_3)_2$ and $Sr_2B_2O_5$ whereas it does occur in SrB_4O_7, SrB_6O_{10} fits within this scheme. Figure 4 shows that SrB_4O_7 has the largest band gap and probably the smallest value for E_{Ff}, and we conclude that that this is the cause for its unique property regarding stabilization of Eu^{2+} and also Sm^{2+}.

When we proceed to Ca- and Sr-based oxides with larger positive values for E_{Ff}, like CaO and SrO, Eu^{2+} is predicted to be less stable. Eu in CaO synthesized under neutral (N_2) atmosphere enters as Eu^{3+} together with a small concentration of Eu^{2+}. Under reducing atmosphere (H_2) the Eu^{2+} concentration increases significantly, but still Eu^{3+} is present. A complete conversion could not be obtained. Similar observations apply to SrO:Eu.[32,33] These two compounds in Figure 4 have E_{Ff} at 1.2 and 1.5 eV, and we conclude that with these high values a complete reduction to Eu^{2+} is not possible anymore.

Returning to the rare earth based oxide compounds, Figure 3 shows that $LaMgB_5O_{10}$, $LaPO_4$, and LaB_3O_6 fall within the boundaries E_{Ff} < 0.7 eV and E_{VC} > 8 eV. Analogous to the Ca-, Sr-, and Ba-based oxides, one might expect to find divalent Eu^{2+} in these wide band gap La-based compounds; especially when prepared in a reducing atmosphere. However, no such finding was reported. It suggests that besides the value for E_{Ff} also the charge of the replaced cation effects the valence stability of the lanthanide impurity. $LaPO_4$ doped with Ce^{3+} and Eu^{3+} does however show the phenomenon of electron transfer from Ce to Eu.[34,35] This indicates that the ground states of Ce^{3+} and Eu^{3+} are close to the Fermi level, and they can easily be converted into Ce^{4+} and Eu^{2+}. The same applies to LaB_3O_6 co-doped with Ce^{3+} and Eu^{3+}.[36]

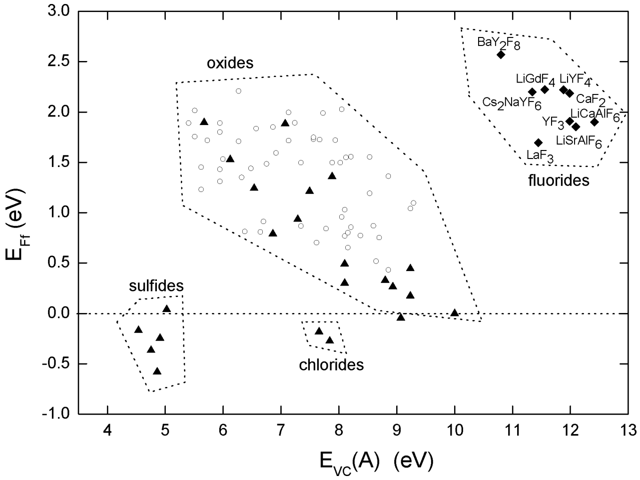

Figure 6. E_{Ff} for Eu^{2+} in oxide, chloride, sulfide, and fluoride compounds. The solid diamond symbols are for Eu in fluoride compounds. Data on the oxide, chloride, and sulfide compounds are the same as in Figure 4.

Figure 4 shows data on E_{Ff} in BaFCl, KCl, and RbCl and several sulfides. For these compounds, E_{Ff} is negative or very close to zero. Eu in BaFCl behaves similar as in compounds such as $BaBPO_5$ and $BaSO_4$ treated above. Eu^{2+} is obtained when prepared in reducing atmosphere (CO), and Eu^{3+} is obtained when prepared in open (air) atmosphere.[37] The Eu^{3+} state is not very stable since it can change it valence to Eu^{2+} in air at high temperature.[2] These observations agree with a value for E_{Ff} close to zero. E_{Ff} of Eu^{2+} is negative in KCl and RbCl, and Eu prefers the divalent charge state. Only after several treatments in air at 500 °C, part of the Eu^{2+} could be oxidized to Eu^{3+}.[38,39]

Figure 4 shows that E_{Ff} for SrS, CaS, and MgS is close to zero, which suggests that one should be able to prepare the materials with Eu^{2+} as well as with Eu^{3+}. CaS:Eu is a thoroughly investigated compound because of its use in luminescence applications. Indeed when prepared in a neutral atmosphere of N_2, Eu enters CaS in both valencies.[40] Depending on the synthetic conditions, samples can be prepared with predominantly Eu^{2+} or with predominantly Eu^{3+}.[41,42] On the basis of the position of the data in Figure 4, similar behavior is expected for SrS and MgS. Figure 4 shows that E_{Ff} becomes increasingly more negative in the sequence $BaGa_2S_4$, $SrGa_2S_4$, to $CaGa_2S_4$. It agrees with the observation that Eu is only known to exist as Eu^{2+} in $CaGa_2S_4$ (see Figure 1).

In Figure 6, information on E_{Ff} in fluoride compounds is shown together with the same data as in Figure 4. E_{Ff} appears larger than 1.5 eV. Despite the large positive value, Eu^{2+} can be stabilized on divalent alkaline earth sites (Ca, Sr, Ba), but reducing conditions are required like synthesis in hydrogen or HF. Information on whether it can also be synthesized

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under oxidizing atmosphere was not found, but from Figure 6 one concludes that the trivalent state is preferred.

The foregoing discussion of data shows that E_{Ff} determines whether a lanthanide ion prefers the divalent or the trivalent charge state. It also indicates the susceptibility of a lanthanide ion to reduction or oxidation. At this stage, two effects of a reducing or oxidizing treatment are envisaged. Generally, a reducing atmosphere during synthesis adds electrons to a compound, and Eu^{3+} is converted to Eu^{2+}. We may illustrate this by a rising of the Fermi energy above level 2 as shown in Figure 2b. On the other hand, an oxidizing atmosphere may lower the Fermi energy to below level 1, and the divalent charge state is converted to the trivalent one as illustrated in Figure 2c. However, there is more. When an electron is added to Eu^{3+} by reducing treatments, negative charge must be removed at other places in the compound in order to maintain charge neutrality. This can be by means of a point defect like an anion vacancy. If it is near Eu, it will further stabilize the divalent state. We may envisage such stabilization by a lowering of levels 1 and 2 to below the Fermi energy as illustrated in Figure 2d. Again level 2 is below E_{F} and Eu^{3+} is converted to Eu^{2+}.

The effect of point defects is evidenced from an observed increase of the $\mathrm{Eu}^{2+}/\mathrm{Eu}^{3+}$ ratio in $\mathrm{Sr_2B_5O_9Cl}$ prepared in air when co-dopants Na^{+}, Sr^{2+} (= no co-dopant), La^{3+}, or Zr^{4+} are used, respectively.[43] Adding K^{+} to $\mathrm{SrB_6O_{10}}$ sharply decreases the $\mathrm{Eu}^{2+}/\mathrm{Eu}^{3+}$ concentration ratio because K^{+} on a Sr^{2+} site acts as a charge compensation for Eu^{3+}.[3] Possibly the effect of a charge compensating ion on E_{Ff} is largest in poorly polarizable compounds with small anions such as in fluorides and oxides. In strongly polarizable lattices with large anions such as in bromides, iodides, and sulfides, the effect is probably smaller due to screening of the Coulomb potential of the charge compensating defect.

At this point of research, it is not known how much the Fermi level can be raised or lowered by means of reducing or oxidizing treatments. Also how much the level locations of the lanthanide ions themselves are shifted by nearby point defects is not precisely known. Probably under reducing conditions both (as illustrated in Figure 2b and d, respectively), occur simultaneously. Despite these unknown aspects, the size of E_{Ff} as determined with the method described in this work does give an indication on the valence stability and clear trends with E_{Ff} are observed.

Summary and Conclusions

From level schemes as in Figure 1 and 5, information is available on the location of the ground state of divalent lanthanides relative to the Fermi energy in wide band gap inorganic compounds. In this work, the relationship between E_{Ff} and the ability to reduce Eu^{3+} to the divalent state or to oxidize Eu^{2+} to the trivalent state was studied. Information available on the redox properties of Eu agree with the trends observed in E_{Ff}. Eu^{3+} is the preferred charge state when $E_{\mathrm{Ff}} > 0$ and when synthesis is under neutral atmosphere. This is the usual situation for Eu on a trivalent rare earth or divalent alkaline earth sites in oxide compounds. Under reducing conditions, Eu^{2+} can be stable on alkaline earth sites but is not found to be stable enough on a trivalent rare earth site in oxide compounds. The charge of the replaced cation (2+ or 3+) is believed to play a role in this. In an interesting group of oxide compounds with alkaline earth sites, Eu can be reduced to Eu^{2+} under synthesis in air at high temperature. A clear correlation with a small value (<0.7 eV) for E_{Ff} was found. In chloride, bromide, and sulfide compounds, $E_{\mathrm{Ff}} < 0$ and Eu^{2+} is predicted and also observed to be the preferred charge state.

The findings for the valence stability of Eu can easily be transferred to predict the valence stability of other lanthanides because E_{Ff} for each lanthanide ion is a fixed amount larger than E_{Ff} for Eu^{2+}. For example, the situation for Sm doped compounds is obtained by simply shifting all data points in Figure 6 upward by 1.2 eV. Un upward shift by 2.1−2.4 eV gives the situation for Er. Clearly it is more difficult to stabilize Sm^{2+} in oxide compounds than Eu^{2+}, and it will be impossible for Er^{2+}.

At this stage, there are still substantial errors in the values for E_{Ff} either because of uncertainties in the energy for charge transfer to Eu^{3+} or uncertainties in the location of the bottom of the conduction band. Also the effects of point defects on level locations are not yet well-known. They will undoubtedly influence E_{Ff} and the stability of the charge state of lanthanides. Nevertheless, E_{Ff} provides one of the few or perhaps even the only quantitative parameter to describe valence stability of lanthanide ions in wide band gap inorganic compounds. Its value has been determined in this work for many different compounds. A phenomenological approach was chosen to identify the main trends. They appear to agree with observation and experience. Quantifying valence stability by means of a measurable parameter (E_{Ff}) provides deeper insight in the underlying physics, and it is hoped that this new approach will initiate more refined studies.

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