Reactions in Crystalline Lattices: Chemistry of Lower Valence States of Lanthanides*

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Reduction of rare-earth (RE) ions to lower valence states in ionic crystals is described in terms of the equilibrium distribution theory for the (alkali halide):RE⁺⁺⁺ and (alkaline-earth halide):RE⁶⁺ systems. Thermoluminescence glow curves of radiation-reduced CaF₂:RE⁺⁺⁺ systems reveal that the roxidation of the divalent ions apparently occurs through thermal excitation of an f electron to the d bands. The additive reduction of RE⁺⁺⁺ to the monovalent state in alkali halides yields striking results: While Sm⁺⁺ ions in KCl obtained by gamma radiation give rise to broad-band optical spectra which were attributed to 4f⁶→4f⁵d₆ transitions, those obtained through high-temperature additive treatment with liquid K give rise to narrow-line spectra that are not easily interpreted. These results illustrate well the major differences between the radiation reduction and additive reduction processes.

I. INTRODUCTION

Alkaline-earth halides and alkali halides are two major classes of ionic crystals which show promise as appropriate host media for redox reactions of the lanthanide (RE) ions. Several detailed investigations into the reduction of RE⁺⁺⁺ ions to the divalent state in CaF₂ and RE⁺⁺ ions to the monovalent state in KCl have been made in the last decade. In both hosts, we are dealing with compensated lattices in which the RE ions are associated with lattice defects characteristic of the hosts. In CaF₂, RE⁺⁺ ions are charge compensated by F⁻ interstitials, while in KCl, RE⁺⁺ ions are accompanied by K⁺ vacancies. The various processes of reduction may be broadly described in terms of two categories: (a) valence reduction by ionizing radiation and (b) valence reduction by chemical means. In the former case, the reduction process is characterized by: (1) the concentration of the reduced ions attainable in the sample of a given total rare-earth content saturates with the radiation dosage; (2) the attainable concentration of reduced rare-earth ions saturates as the total rare-earth content increases; and (3) the reduced ions thus obtained are relatively unstable. The reversion of these ions to the original oxidation state occurs readily with brilliant thermoluminescence when the samples are heated above the irradiation temperature. These observations have been considered to be consistent with the postulate that only rare-earth ions unassociated with charge compensation can trap electrons to give reduced rare-earth ions. The instability of the divalent rare-earth ions is ascribed to the fact...
that trapped hole centers are produced simultaneously with the trapping of electrons on the RE impurities. In case (b) the RE ions are reduced when the samples are heated in the vapor or liquid of the corresponding metal of the host cation at elevated temperatures. Alternatively, when the samples are subjected to an electric field at elevated temperatures, the RE impurities are electrochemically reduced. In both cases the reduced species appear to be stable thermally and optically. The stability of the chemically or electrochemically reduced species is attributable to the fact that the compensation defects are removed from the crystal lattice during the reduction process.

The concepts outlined above represent generalized current interpretations of the reduction phenomena in compensated lattices. While they give plausible explanations to many of the observations, they are somewhat vague in several important details. The postulate that only RE ions in dissociation from compensation defects are reduced in radiation experiments implies the association–dissociation equilibrium involving the RE ion and the compensation defect.\(^{10,12}\)

**RE ion – compensation defect complex**

**RE ion + compensation defect.**

Just what is meant by a RE ion in dissociation from its charge compensation? In fact, recent papers from this laboratory\(^{13–14}\) have conclusively shown that RE ions and lattice defects in compensated lattices are virtually all paired within the first few nearest-neighbor positions at appropriately low temperatures.\(^{14,17,19}\) It is the purpose of the present paper to examine the basic features of the reduction processes of RE ions to lower valence states in ionic crystals in terms of our recent findings concerning the compensated lattices. In this connection, thermoluminescence experiments involving 11 different CaF\(_2\):RE\(^{3+}\) systems have been conducted. Also, the reduction of Sm\(^{3+}\) and Eu\(^{3+}\) to the monovalent state has been carried out by high-temperature additive treatment of KCl:Sm\(^{3+}\) and KCl:Eu\(^{3+}\) samples with liquid K. The results are totally different from those previously obtained for KCl:Sm\(^{3+}\) in \(\gamma\)-irradiation experiments.\(^{11}\) Instead of the unstable broad-band absorption spectra (identified as \(4f^76s^1 \rightarrow 4f^76s^2\) transitions in Sm\(^{3+}\)) previously observed,\(^{11}\) a completely new spectrum of narrow lines (observed only at 4.2\(^\circ\)K) is obtained in the additively treated samples.

**II. DISTRIBUTION LAWS IN COMPENSATED LATTICES**

The law of equilibrium distribution which governs the low-temperature pair formation of divalent cations and cation vacancies in alkaline halides\(^{14}\) and that of trivalent cations and interstitial anions in alkaline-earth halides\(^{17}\) has been useful in the interpretation and prediction of spectroscopic data on compensated lattices.\(^{15–18}\) In which alloivalent cations and lattice defects (which may be thought of as anions) interact as ions of opposite unit charges in a crystalline solution. In general, \(N_i\) unipositive ions and \(N_i\) uninegative ions give rise to a total interaction energy, for a given configuration,

\[
U(\tilde{R}_1, \tilde{R}_2, \ldots, \tilde{R}_{2N_i}) = \sum_{l \leq k \leq N_i} u(\tilde{R}_{lk}) + \sum_{N_i + 1 \leq l \leq 2N_i} u(\tilde{R}_{ln}) + \sum_{N_i + 1 \leq l \leq 2N_i} u(\tilde{R}_{lk})
\]

(1)

where \(\tilde{R}_1, \tilde{R}_2, \ldots, \tilde{R}_{2N_i}\) are the position vectors of the \(N_i\) cations and \(N_i\) anions, and \(+u\) and \(-u\) denote repulsive and attractive interaction energies, respectively. At low temperatures at which only the attractive terms are important, it has been shown that the canonical configuration partition function,

\[
Z = \sum_{\text{all configuration}} \exp[-U(\tilde{R}_1, \tilde{R}_2, \ldots, \tilde{R}_{2N_i})/kT]
\]

(2)

reduces to a product of “molecular” pair partition functions, such that\(^{14}\)

\[
Z \approx \left(\sum_{l=l'} g_l \exp\left(-\frac{-u(R_l)}{kT}\right)^{N_i}\right) = q_p^{N_i}
\]

(3)

where \(g_l\) is the number of equivalent positions at which a defect (i.e., a uninegative ion) can be situated about an alloivalent cation (i.e., a unipositive ion) at a separation distance of \(R_l\). The index \(l\) denotes the number of nearest-neighbor separation, with \(R_l = (2l)^{1/2}\) in alkaline halides\(^{14}\) and \(R_l = (2l - 1)^{1/2}\) in alkaline-earth halides,\(^{17}\) a being a characteristic lattice parameter for the host crystal.\(^{14,17}\) The sum over \(l\) is carried from \(l = 1\) to \(l = l'\), where \(l'\) is arbitrarily chosen such that \(q_p\) does not change appreciably in summing beyond \(l'\). At a given temperature for which Eq. (3) is valid, the number \(n_{l}\) of pairs of separation \(R_l\) is

\[
n_{l} = N \tilde{q}_p^{N_i} g_l \exp[-u(R_l)/kT]
\]

(4)

which has been shown to be the case in the KCl:Sm\(^{3+}\)\(^{14,16}\) and the CaF\(_2\):RE\(^{3+}\)\(^{17}\) systems at appropriately low temperatures. At high temperatures at which the ion-defect pairs dissociate to an appreciable extent, Eqs. (3) and (4) become meaningless as we must include the repulsive terms in Eq. (1) in our evaluation of \(Z\).

At high temperatures when repulsive as well as attractive interactions are taken into consideration, we arrive\(^{16}\) at the expression for configuration partition function,

\[
Z = \Omega_0(2N_i, N) \left[1 + \frac{[N_i/(N - 1)]}{\sum_{j} \exp[-u(R_j)/kT]}ight] - 1
\]

\[
+ \sum_{p} g_p \exp[-u(R_p)/kT] - 1
\]

\[
= \Omega_0(2N_i, N) e^{N_i}
\]

(5)

which in the limit of vanishing values for \(+u\) and \(-u\), reduces to the random mixing factor \(\Omega_0(2N_i, N)\) for
distributing $N_i$ RE ions and $N_i$ compensation defects on $N$ available sites. Equation (5) is correct for $N_i/N \ll 1$. It leads to the expressions for $n_i^+$ and $n_i^-$, the total number of repulsive and attractive pair interactions at $R_i$, respectively,

$$
\pm n_i^\pm = \left[ N_i^\pm / (N-1) \right] G(R_i)
= \left[ N_i^\pm / (N-1) \right] g_i \exp \left( \mp u_i/kT \right).
$$

Detailed calculations for KCl:Sm$^{3+}$4 employing Eq. (4) show that at low temperatures ($T \leq 500^\circ$K), all the Sm$^{3+}$ ions are paired with K$^+$ vacancies. The dominant pairs, in the order of their relative importance, are the $C_4$$(2, 0, 0)$, $C_6$$(2, 1, 1)$, $C_8$$(1, 1, 0)$, $C_1$$(3, 2, 1)$, $C_6$$(3, 1, 0)$, $C_8$$(2, 2, 0)$, and $C_8$$(2, 2, 2)$ pairs [where the notations $C_4$, $C_6$, $C_8$, and $C_1$ denote the site symmetry of the Sm$^{3+}$ ion, and the integers in parentheses, e.g., $(2, 0, 0)$, give the lattice position of the vacancy with Sm$^{3+}$ at the origin $(0, 0, 0)$, with the lattice constant for approximately 90% of the Sm$^{3+}$ ions in CaF$_2$:RE$^{3+}$ systems, the situation is very similar$^{8}$. The dominant RE$^{3+}$–F$^-$ interstitial pairs at $T \leq 700^\circ$K are the $C_4$$(1, 0, 0)$, $C_6$$(2, 0, 0)$, $C_8$$(1, 1, 0)$, $C_1$$(1, 2, 2)$, $C_1$$(1, 3, 0)$, $C_6$$(2, 3, 0)$, and $C_8$$(3, 0, 0)$ sites, again with the first three accounting for the majority of the RE$^{3+}$ ions. There appears to be little doubt that, contrary to earlier thinking, radiation reduction does not involve RE ions in dissociation from their compensation defects.

Calculations for the high-temperature ($T \geq 900^\circ$K) case employing Eq. (6) lead to the conclusion that pair formation of RE$^{3+}$ and F$^-$ interstitials is not important. At $T=900^\circ$K and $N_i=10^{17}$ cm$^{-3}$, only $2 \times 10^{15}$ cm$^{-3}$ ion-defect pairs are within $l \leq 21$. Thus, in additive reduction processes carried out at elevated temperatures, we are primarily dealing with RE ions in dissociation from the associated defects. Interactions between the RE ions and their compensation can thus be neglected to a first approximation.

In the following sections, we shall outline (a) the reduction processes by ionizing radiation and (b) the reduction process by high-temperature additive treatment in terms of the discussions detailed in the present section.

III. RADIATION-INDUCED REDUCTION AND THERMOLUMINESCENCE

In view of the discussions in Sec. II, it appears that the association–disassociation hypothesis of radiation-induced reduction of RE ions to lower valence states is incorrect. Instead, we must take into consideration the presence of a distribution in RE ion-defect pairs. Take the example of a CaF$_2$:RE$^{3+}$ system. The binding energies of the first three nearest-neighbor (nn) RE$^{3+}$–F$^-$ interstitial pairs are $\approx -0.48$, $-0.30$, and $-0.35$ eV, respectively. If the RE$^{3+}$ is reduced to the divalent state through trapping of an electron, the RE ion would lose the stabilization energy due to the attraction of the trivalent cation to the F$^-$ interstitial. From this point of view, it is clear that the nn $C_4$(1, 0, 0) RE$^{3+}$–F$^-$ interstitial pair, having the greatest stabilization energy due to pairing, would be the most resistant to reduction. On this basis, too, we would expect that the radiation-reduced RE$^{3+}$ ions would exist in several site symmetries insofar as they arise from RE$^{3+}$ ions in a multiplicity of sites. In pursuing this interpretation, we have carried out a set of thermoluminescence experiments involving 11 different CaF$_2$:RE$^{3+}$ systems. These experiments are reported in the following.

Experiment on Thermoluminescence of Irradiated CaF$_2$:RE$^{3+}$

The CaF$_2$ crystals doped with 0.05 mol % RE$^{3+}$ ions, (Optovac, Incorporated) were irradiated for 48 h with gamma rays from a cobalt-60 source which emits at a rate of approximately $0.5 \times 10^8$ rad/h. In a specially designed aluminum block furnace, the reduced crystals were heated at a controlled rate of $10^6$ min$^{-1}$ by a Melabs Temperature Programmer Model C111 and a Melabs Proportional Temperature Controller Model CTC-1A. A Chromel–Alumel thermocouple was employed to measure the temperature change from about 20–450°C. The furnace was placed in a bronze jacket with a quartz window which was connected to a photomultiplier tube (RCA 7265) with an S-20 response. A dry-ice housing and a light-tight joint were used to connect the jacket to the photomultiplier tube. The signal of the photomultiplier tube, which measures the thermoluminescence intensity of emission characteristic$^{4,12}$ of the RE$^{3+}$ ions, was plotted versus the increasing temperature measured as a millivolt output of the thermocouple (monitored by a Leeds–Northrup potentiometer) on an $X$–$Y$ recorder.

The thermoluminescence glow curves of Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, and Gd$^{3+}$ are shown in Fig. 1. The glow curves of Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, and Tm$^{3+}$ are shown in Fig. 2. The prominent features of these glow curves are: (1) the striking dependence of the glow curves characteristics on the nature of the RE ion, and (2) the presence of several multipeaked glow curves in one single CaF$_2$:RE$^{3+}$ system. The nonobservance of a Eu$^{3+}$ glow curve in the temperature range of our experiments, the temperature range of our experiments, indicates the thermal stability of the 4$f^7$ configuration. The dependence of the glow characteristics on the nature of the RE ion suggests that the thermal oxidation process,

$$
\text{RE}^{3+} \rightarrow \text{RE}^{3+} + \text{electron},
$$

is responsible for the thermoluminescence glow, which is not the case in low-temperature glow experiments.$^{20}$ The details of the electron release process are not known. However, we propose to show that such a process probably takes place through excitation of the RE$^{3+}$ ion from the 4$f^7$ configuration to the 4$f^6$–15d$^1$ configuration. From standard arguments,$^{13}$ we estimate that the glow peaks observed in Figs. 1 and 2 correspond to trap
depths in the range 1–2 eV. The estimated energies corresponding to the first glow peaks of the various RE species are compared (in Fig. 3) with the crystal-field calculations of the onset of the $4f^m \rightarrow 4f^{m-1}5d$ transitions, and with the observed onset of the corresponding optical $f \rightarrow d$ absorption bands. The fit leaves much to be desired. Nevertheless, the fact that the onset of the thermal glow curves occurs in the same energy region as that of the $f \rightarrow d$ absorption bands is suggestive of the involvement of the $d$ bands in the thermal glow processes. Also encouraging is the notable agreement between the optical and thermal data in the high values of Ce$^{3+}$, Eu$^{3+}$, and Tm$^{3+}$ (Fig. 3).

The observation of multiple glow curves in a CaF$_2$: RE$^{3+}$ sample suggests the presence of multiple electron traps. That this is the case in CaF$_2$:Sm$^{3+}$ is shown in the experiment in which the sample was heated at a uniform rate of 10$^5$ min$^{-1}$ to 197°C with the corresponding observation of the first multi-peaked glow curve [Fig. 4(a)]. The sample was subsequently cooled to 20°C. Upon reheating the same sample under identical conditions, the first glow curve was not observed. Only the

![Diagram](image1)

**Fig. 1.** Thermoluminescence glow curves of CaF$_2$ crystals containing Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, and Gd$^{3+}$ ions produced by room-temperature $\gamma$ irradiation. The heating rate was 10$^6$ min$^{-1}$.

![Diagram](image2)

**Fig. 2.** Thermoluminescence glow curves of CaF$_2$ crystals containing Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, and Tm$^{3+}$ ions produced by room-temperature $\gamma$ irradiation. The heating rate was 10$^6$ min$^{-1}$.

![Diagram](image3)

**Fig. 3.** Comparison of estimated trap-depth energies (○) corresponding to the first glow peaks of the radiation produced CaF$_2$:RE$^{3+}$ crystals with the crystal-field calculations (□) of the onset of the $4f^m \rightarrow 4f^{m-1}5d$ transitions, and with the observed onset of the corresponding optical $f \rightarrow d$ absorption bands (△). The point for Eu$^{3+}$ represents the lower limit.

higher-temperature glow curve was observed when the sample was heated to 371°C [Fig. 4(b)]. This observation conclusively shows the presence of at least two different sites, both of which contribute to thermoluminescence. The fine structure observed in the two major glow curves of CaF$_2$:Sm$^{3+}$ could arise from either (a) a number of sites closely spaced in energy or (b) a number of different excited levels available to one and the same site. Details of the analysis which determines one of these two possibilities will be published at a later date.

The observation of more than one Sm$^{3+}$ site in the $\gamma$-irradiated CaF$_2$:Sm$^{3+}$ system by the above experiment is in agreement with the expectations described earlier in terms of the site distribution theory. Con-
firmation of this point can be obtained through detailed ZAF (Zeeman anisotropy fluorescence) spectroscopic investigations into the site symmetries of the Sm\(^{2+}\) ions in the manner previously described\(^{13,15,16}\) for the KCl: Sm\(^{2+}\) system.

IV. ADDITIVE REDUCTION

When an alkaline-earth halide (MX\(_2\)) crystal containing trivalent rare-earth ions is heated in the corresponding alkaline-earth metal vapor at sufficiently high temperatures (>750°C), the rare-earth ions are readily reduced to the divalent state as the charge compensation anion interstitials are removed from the crystalline lattice to form additional MX\(_2\) layers on the crystal surface. Valence reduction of this type may be described by a reaction cycle similar to that outlined previously.\(^{12}\) The energy \(U\) required or gained by the additive reduction process can be empirically determined from simple equilibrium considerations.\(^{19}\) The free energy of a monatomic vapor of M containing \(n_1\) atoms per unit volume may be written as

\[
F_v = -n_1kT[\log[(2\pi mkT/h^2)]^{3/2} + \log(n_1)^{-1} + 1].
\]

(7)

The change in free energy caused by the removal of one atom from the vapor is

\[
\Delta F_v = kT[\log[(2\pi mkT/h^2)]^{3/2} + \log(n_2)^{-1}].
\]

(8)

At high temperatures at which \(kT\gg \mu_4\) for most important values of \(l\), we can neglect the configuration-interaction energy described in Sec. II. Since for every M atom that settles on the crystal, two R\(^{2+}\) ions are reduced according to the equation,

\[
M + 2R^{2+} = M^{2+} + 2R^{2+},
\]

we have \(1/2n_2\) excess M\(^{2+}\) ions if there exist \(n_2\) R\(^{2+}\) ions in the crystal. The entropy of the system is, if there are \(n_1\) R\(^{2+}\) ions,

\[
S = k\log[(N + 1/2n_2 + n_2 + n_1)/(N + 1/2n_2)!n_2!n_1!],
\]

(9)

where \(N\) is the original number of MX\(_2\) molecules. When the number of excess M\(^{2+}\) ions increases by one, the change in entropy is

\[
\Delta S = k\log[(N + 1/2n_2 + n_2 + n_1 + n_2)/(N + 1/2n_2 + n_2)!n_2!n_1!]
\]

(10)

The increase in free energy in the crystal is thus

\[
\Delta F_v = -U - kT\log[(N + 1/2n_2 + n_2 + n_1 + n_2)/(N + 1/2n_2 + n_2)!n_2!n_1!].
\]

At equilibrium

\[
\Delta F_v + \Delta F_v = 0,
\]

(12)

and we obtain

\[
\frac{(N + 1/2n_2)n_2^2}{(N + 1/2n_2 + n_2 + n_1)n_2^2} = n_1\left(\frac{2\pi mkT}{h^2}\right)^{-3/2} \exp\left[-\frac{U}{kT}\right].
\]

(13)

For \(N\gg n_1\), and setting \(n_2 + n_1 = n_0\), which is constant,

\[
\kappa = \frac{n_2}{n_0^{3/2}} = \frac{(N+n_0)}{N}\left(\frac{2\pi mkT}{h^2}\right)^{-3/2} \exp\left[-\frac{U}{kT}\right],
\]

(14)

where \(\kappa\) is the equilibrium constant for the reduction process, and \(n_1\), \(n_2\), and \(n_0\) are measurable quantities.

The basic features of the additive reduction process are thus different in a fundamental way from those of the radiation-induced reduction process discussed in Sec. III. In the latter process, practically all the RE ions undergoing valence reduction are in close proximity of the compensation defects. In an additive reduction process, however, the influence of the compensation defects on the RE ions involved is in fact quite unimportant. Despite this basic difference, both ionizing radiation and additive treatments of CaF\(_2\):RE\(^{2+}\) systems lead to RE\(^{2+}\) ions the spectroscopic properties of which apparently have little to do with the method of preparation.\(^{14}\) In the following experiment, we shall show that such is not the case when RE\(^{2+}\) ions are reduced to the monovalent state in KCl.

Experiment on the Additive Reduction of KCl: Sm\(^{2+}\) and KCl: Eu\(^{2+}\)

Single crystals were grown from KCl melts containing 0.1 mol % Sm\(^{2+}\) and Eu\(^{2+}\) ions by the Czochralski method.\(^{11}\) The resulting KCl: Sm\(^{2+}\) and KCl: Eu\(^{2+}\) crystals were analyzed by EDTA (ethylene diamine tetra-acetic acid) determinations and found to contain 0.0042±0.0002 and 0.0097±0.0004 mol % Sm\(^{2+}\) and Eu\(^{2+}\) ions, respectively. The additive pressure treatments were made by immersing the crystal specimen in liquid K contained in a Ta cylinder which is simultaneously heated and compressed in a piston apparatus.\(^{22}\) The pressure on the specimen was hydrostatic. The specimen was equilibrated with the K liquid at 650°C and pressures to 17 kbar. After equilibration, the assembly was quenched to 200°C or less under pressure.
in about 30 sec. The pressure and temperature were then decreased together so that the K ambient remains liquid until a pressure of 1 atm was attained. The absorption spectra of the resulting specimens were then measured on a Cary 14 spectrophotometer at 77 and 4.2 K.

The absorption spectra thus obtained at 77 K show the well-characterized bands for the F, R₁, R₂, M, and N centers and are indistinguishable from those of a "pure" KCl crystal which has been similarly treated. At 4.2 K, a set of hitherto unreported lines, in addition to the usual color center absorption, are observed in the 1–2-μ region in the KCl:Sm²⁺ and KCl:Eu²⁺ crystals (Fig. 5). As the pressure of the additive treatment increases, the optical densities of all the lines of either RE specimen increase uniformly at the same rate, indicating that they arise from the same origin. These observations establish the fact that the observed line spectra must arise from the reduction of the rare-earth ions to some lower valence state, since they do not belong to the divalent ions, and oxidation of the RE ions to some higher valence state is not only unlikely under additive conditions, but also energetically impossible due to the vanishingly low solubility of trivalent ions in KCl.

The monotonic increase in the concentration of the reduced rare earth with pressure is shown in Fig. 6. This pressure dependence is consistent with the expectation that the RE²⁺ ions have been reduced to the monovalent state. According to the above discussion, the reduction of an impurity ion to the valence state characteristic of the host ion is accompanied by the elimination of the associated charge compensation. If the charge compensation is a vacancy as in the present case, the reduction process results in a lower partial molar volume. Such a process is thus favored at high pressures, as the reduced rare-earth ion assumes the cubic site symmetry of the K⁺ lattice ion in the absence of a K⁺ vacancy.

The pressure dependence of the equilibrium constant ν can be expressed in terms of the atomic volumes of the reactants and the products in the equations,

$$kT (∂/∂p) \ln κ = \sum \bar{v}_T - \sum \bar{v}_P,$$

(15)

where \(\bar{v}_T\) and \(\bar{v}_P\) are the atomic volumes of the reactants and the products, respectively. The reduction of the RE²⁺ ion to the monovalent state may be represented by the equation

$$\text{RE}^{2+} + V_{K^+} \rightarrow \text{RE}^{3+} + K^{+};$$

(16)

where \(V_{K^+}\) denotes a K⁺ vacancy, which leads to the relationship for the pressure dependence of the equilibrium constant of the reaction:

$$kT (∂/∂p) \{ 2 \ln [\text{RE}^{2+}] - 2 \ln (N_T - [\text{RE}^{2+}]) \}$$

$$= \bar{v}_{\text{RE}^{2+}} + \bar{v}_{V_{K^+}} + \bar{v}_{K^{+}} - \bar{v}_{\text{RE}^{3+}} - \bar{v}_{K^{+}}$$

$$= \bar{v}_{K^{+}} = 65 \text{ Å}^3,$$

(17)

where \(N_T\) is the total rare-earth concentration. The last approximate equation sign is valid in light of the finding that in the KCl:Ca²⁺ system, the volume occupied by the Ca²⁺+K⁺ vacancy is roughly 80% that occupied by two K⁺ ions. The ionic radius of Ca²⁺ is
0.99 Å and that of RE⁺ is 1.21 Å. The larger size of the RE⁺ ion suggests that the volume occupied by the RE⁺-K⁺ vacancy pair would even be closer to that occupied by the two corresponding K⁺ ions. The RE⁺ ion is somewhat smaller than the K⁺ ion (the ionic radius of which is 1.33 Å). The RE⁺ ion, on the other hand, is expected to be close to or slightly larger than the size of the K⁺ ion. In any event, we have $\varphi_{RE^+ - K^+} \approx \varphi_{RE^+} + \varphi_{K^+}$, and Eq. (17) is obtained.

In Eq. (17) the terms

$$(\partial/\partial \rho) \ln[RE^+] \text{ and } (\partial/\partial \rho) \ln(N-[RE^+])$$

must take on opposite signs, since RE⁺ is obtained at the expense of RE⁺. Since their difference is positive as shown in Eq. (17), the term $(\partial/\partial \rho) \ln[RE^+]$ must be positive. That is, the production of the RE⁺ must increase with increasing pressure, which is indeed the case in our experimental observation (Fig. 6).

In a recent investigation, the reduction of Sm³⁺ to the monovalent state in KCl by $\gamma$ irradiation resulted in a weak broad-band spectrum (not observed in the present investigation) in the near infrared which has been attributed to the transition $4f^66s^2 \rightarrow 4f^56s^3$, with $4f^66s^3$ as the ground configuration of the Sm⁺ ion. No narrow-line absorption of the type shown in Fig. 5 was observed. The question thus arises: If both the irradiation procedure and the present additive treatment result in the Sm⁺ + e⁻ → Sm⁺ reduction processes, how do we reconcile the narrow-line spectrum observed in our present study with the broad-band spectrum of the earlier investigation? The answer to this question has been hinted at above: When Sm³⁺ ions enter the KCl lattice, an equal number of charge compensation K⁺ vacancies are formed. At low temperatures and concentrations, there exists a Maxwell-Boltzmann distribution of Sm³⁺:K⁺ vacancy pairs consistent with the interactions which stabilize such pairs. All Sm³⁺ ions are in close association with K⁺ vacancies at ordinary temperatures. Reduction caused by room temperature ($\sim 300$°K) irradiations, therefore, most probably leads to the creation of Sm⁺ ions in close association with K⁺ vacancies predominantly in the $C_{1z}(2,0,0)$, $C_{1y}(2,1,1)$, and $C_{2z}(1,1,0)$ configurations. In our present investigation, on the other hand, since the compensation K⁺ vacancies are eliminated from the lattice during the additive reduction, the resulting monovalent ions are in an octahedral environment. If these interpretations are correct, we are led to the conclusion that the remarkable difference in the absorption properties of Sm⁺ obtained by $\gamma$ irradiation and by the present technique appears to originate from the difference in the RE ion site symmetry.

The behavior reported above is probably a result of the ever-decreasing energy separations between electronic configurations of the RE ion as the effective nuclear charge decreases with lowering valence states. In monovalent RE ions, the low-lying ground configurations are expected to be close-by energetically. The anomaly which we observe here may well be a manifestation of the fact that the crystalline fields are large compared to the configuration energies of the RE⁺ ion. Crystal-field effects on the various configurations in rare earths can vary over several orders of magnitude. For example, in the $f^6$ configuration they are $\sim 10^9$ cm⁻¹, whereas in the $f^{5-7}d^1$ configuration, they are $\sim 10^6$ cm⁻¹. The site symmetry, therefore, can play a dominant role on the configuration character of the RE⁺ ground state if several low-lying configurations fall within the range of the crystal-field effects. The results reported above provide an interesting topic for future theoretical investigations.

An attempt was made to extend our present investigations to lanthanides other than Sm and Eu. However, we have consistently failed to obtain samples containing sufficient concentrations of divalent ions other than Sm²⁺ and Eu²⁺. Apparently, even the relatively stable Tm²⁺ ions are substantially oxidized, during our sample preparation, to the trivalent state which is insoluble in the KCl lattice. Unless we have a method of stabilizing the divalent state of rare-earth ions during the crystal-growth process, it appears as though the investigation of the monovalent state of the lanthanide elements will be limited to samarium and europium.

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