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Determination of local distortions around Sm^{2+} in CaFCl from fluorescence studies under pressure

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Abstract. The energy level scheme of Sm^{2+} in CaFCl is determined in detail from the fluorescence spectra of the $^5\text{D}_J \rightarrow ^7\text{F}_J$ transitions at ambient pressure and under pressures up to 8 GPa. The crystal-field (CF) parameters B_q^k are derived directly from CF energy levels and their variations under pressure. The comparison of the CF interactions for Sm^{2+} in different MFCl ($M = \text{Ba}, \text{Sr}, \text{and Ca}$) host crystals shows very similar behaviour under pressure. With the superposition model (SM), the local structure around the Sm^{2+} ions in the CaFCl host is quantitatively determined and the four local structural parameters for the local coordination and the atom positions as well as their pressure dependences are derived. It is thus shown that the present method results in a valuable tool for the investigation of local distortions around optically active impurities.

1. Introduction

When impurity ions are substitutionally embedded in a host crystal, the difference in size between the substituted host ion and the impurity leads usually to a local distortion of the host lattice. Many theoretical and experimental studies have been devoted to this subject. Since the crystal field (CF) interactions for lanthanide ions are successfully described by the superposition model (SM), which relates energy levels to crystal structures, this model offers a particularly useful tool to determine the local structure around the lanthanide ions in different hosts.

Ternary PbFCl-type compounds MFX ($X = \text{Cl}, \text{Br}, \text{or I}$) are suitable host crystals for divalent impurity ions. EPR measurements on Mn^{2+} and Eu^{2+} in SrFCl were performed to study their local distortions [1]. In a previous study [2], the distance dependences of the CF interactions for both $\text{Sm}^{2+}-\text{Cl}^-$ and $\text{Sm}^{2+}-\text{F}^-$ ion pairs in BaFCl and SrFCl hosts have been determined in detail by high-pressure measurements. The same technique is applied here to CF effects on Sm^{2+} in CaFCl, and a comparison of the CF effects in this host series allows us now to derive within the SM the local structural parameters for Sm^{2+} in CaFCl.

2. Experiments and results

2.1. Experimental techniques

$\text{Sm}^{2+}:\text{CaFCl}$ samples were grown with a nominal concentration of 0.1 mol% Sm^{2+} according to the standard Bridgman-technique in the materials laboratory of the University Paderborn.

The fluorescence measurements were performed at low temperature and high pressure with the gasketed diamond anvil cell (DAC) technique and the spectrometer system

described previously in detail [2]. In addition, a dye laser system (Coherent CR-599) pumped by multilines of an argon ion laser (Coherent Innova 70-2) was used to excite directly the 5D_1 multiplet of Sm^{2+} in CaFCl, and, for this purpose, the system was equipped additionally with a special monochromator, a He-Ne laser and a CCD detector to determine the wave number for the dye laser line. This system has a precision of better than 1 cm^{-1} for measurements of excitation spectra.

Spectroscopic poly(chlorotrifluorethylene) oil was used as pressure transmitting medium due to the hygroscopic nature of the CaFCl crystals.

2.2. Fluorescence at ambient pressure

Fluorescence spectra of Sm^{2+} :CaFCl were measured at first at 20 K and ambient pressure. 16 groups of lines in the spectral range from $11\,500\text{ cm}^{-1}$ to $18\,000\text{ cm}^{-1}$ were observed and attributed to the $^5D_2 \rightarrow ^7F_{0-3}$, $^5D_1 \rightarrow ^7F_{0-6}$, and $^5D_0 \rightarrow ^7F_{0-4}$ transitions.

Sm^{3+} fluorescence in CaFCl was also noticed in the spectral range from $14\,000\text{ cm}^{-1}$ to $18\,000\text{ cm}^{-1}$, probably corresponding to the $^4G_{5/2} \rightarrow ^6H_{5/2-11/2}$ transitions. Fluorescence measurements on individual crystals show inhomogeneous distributions of Sm^{3+} in the samples. Different Sm^{3+} centres were observed by the use of different argon ion laser lines. As an example, figure 1 shows two typical spectra excited by the 488.0 nm and 514.5 nm laser lines, respectively.

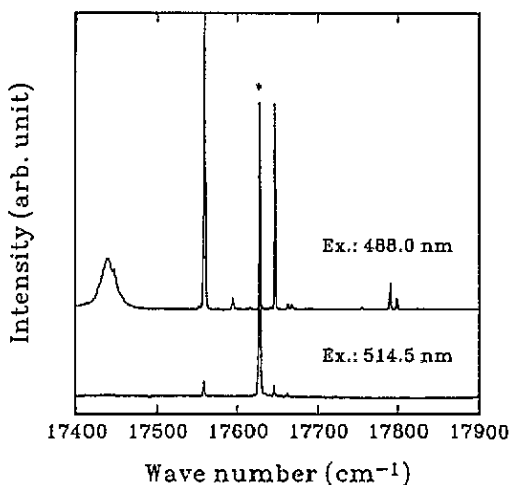


Figure 1. Fluorescence spectra of Sm^{2+} and Sm^{3+} in CaFCl at 20 K and ambient pressure, excited by two different laser lines with wavelengths 488.0 nm and 514.5 nm. The fluorescence line marked by the asterisk is attributed to Sm^{2+} .

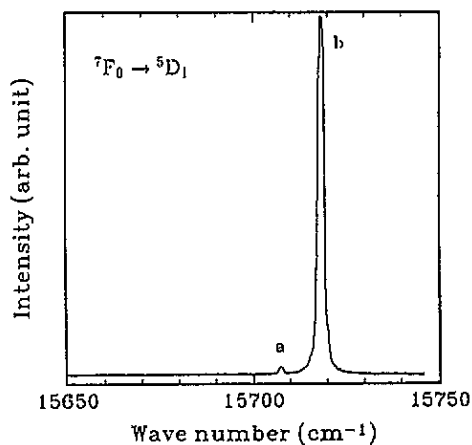


Figure 2. Excitation spectrum of $^7F_0 \rightarrow ^5D_1$ for Sm^{2+} :CaFCl at 20 K and ambient pressure. The lines a and b correspond to $^7F_0 \rightarrow ^5D_1(A_2)$ and $^7F_0 \rightarrow ^5D_1(E)$, respectively.

In order to identify the fluorescence lines from Sm^{2+} and Sm^{3+} ions, the dye laser system was used only to excite the Sm^{2+} ions. Thereby, the dye DCM allowed us to scan the complete spectral region of the $^7F_0 \rightarrow ^5D_1$ transition. Figure 2 shows the excitation spectrum for this region at 20 K and ambient pressure. The two lines a and b represent the transitions $^7F_0 \rightarrow ^5D_1(A_2)$ and $^7F_0 \rightarrow ^5D_1(E)$, which determine the two CF levels of 5D_1 . Under selective excitation with the dye laser line b, the fluorescence spectra of the transitions $^5D_{0,1} \rightarrow ^7F_J$ can be unambiguously identified.

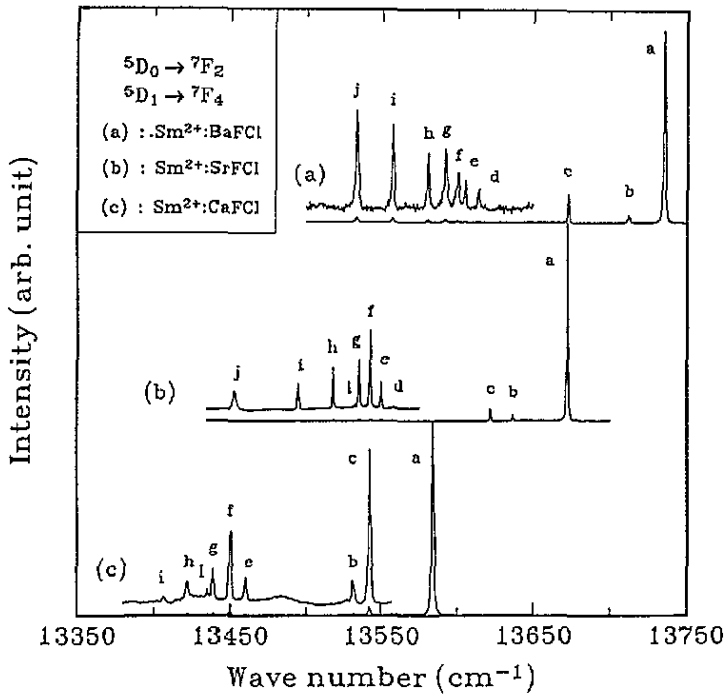


Figure 3. Fluorescence spectra of ${}^5D_1 \rightarrow {}^7F_4$ and ${}^5D_0 \rightarrow {}^7F_2$ for (a) $\text{Sm}^{2+}:\text{BaFCl}$, (b) $\text{Sm}^{2+}:\text{SrFCl}$, and (c) $\text{Sm}^{2+}:\text{CaFCl}$ at 20 K and ambient pressure with the following line assignments:

- | | | |
|---|--|--|
| a: ${}^5D_0(A_1) \rightarrow {}^7F_2(E)$ | b: ${}^5D_0(A_1) \rightarrow {}^7F_2(A_1)$ | c: ${}^5D_1(E) \rightarrow {}^7F_4(A_1)$ |
| d: ${}^5D_1(E) \rightarrow {}^7F_4(E)$ | e: ${}^5D_1(A_2) \rightarrow {}^7F_4(E)$ | f: ${}^5D_1(E) \rightarrow {}^7F_4(E')$ |
| g: ${}^5D_1(A_2) \rightarrow {}^7F_4(E')$ | h: ${}^5D_1(E) \rightarrow {}^7F_4(A'_1)$ | i: ${}^5D_1(E) \rightarrow {}^7F_4(B_2)$ |
| j: ${}^5D_0(E) \rightarrow {}^7F_2(B_1)$ | i: ${}^5D_1(A_2) \rightarrow {}^7F_4(A_2)$ | |

The fluorescence of $\text{Sm}^{2+}:\text{CaFCl}$ shows very similar features to the spectra of $\text{Sm}^{2+}:\text{BaFCl}$ and $\text{Sm}^{2+}:\text{SrFCl}$. As an example, the spectra of the two transitions ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_1 \rightarrow {}^7F_4$ at 20 K and ambient pressure are shown in figure 3 for these three different hosts. Large red-shifts of all the lines can be noticed in the series from BaFCl to CaFCl, but the patterns are very similar, which already allows for an unambiguous assignment of all the lines to crystal field levels. Furthermore, additional polarization measurements on $\text{Sm}^{2+}:\text{CaFCl}$ were performed for cross checking with the earlier results for $\text{Sm}^{2+}:\text{BaFCl}$ [3] and $\text{Sm}^{2+}:\text{SrFCl}$ [4].

According to these results, all the observed spectra could be assigned and a semiempirical approach had to be used only for the CF levels of the ${}^7F_{5,6}$ multiplets, whereby, at first, the CF parameters were derived from the 7F_J ($J \leq 4$) levels and the calculated energy levels were then taken into account for the line assignments of the observed ${}^5D_1 \rightarrow {}^7F_{5,6}$ spectra. Figures 4(a)–(f) illustrate the ${}^5D_J \rightarrow {}^7F_J$ spectra of $\text{Sm}^{2+}:\text{CaFCl}$ at 20 K and ambient pressure together with the corresponding transition diagrams.

38 CF levels were deduced from all the fluorescence spectra as listed in table 1. The ${}^5D_2(A_1)$ level of the four 5D_2 CF levels was not observed; however, from the pressure shifts of the four 5D_2 CF levels of Sm^{2+} in BaFCl and SrFCl (also see [2]), one can already expect that an accidental degeneracy between ${}^5D_2(A_1)$ and ${}^5D_2(E)$ appears in the case of $\text{Sm}^{2+}:\text{CaFCl}$ just at ambient pressure.

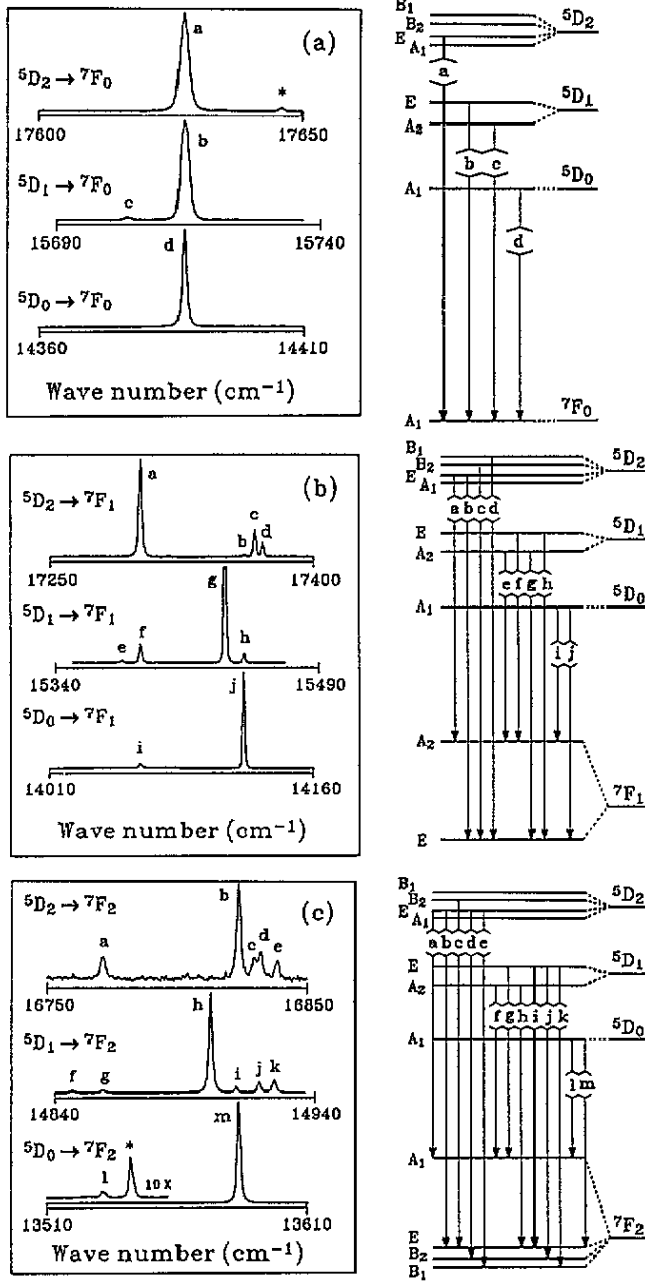


Figure 4. ${}^5D_J \rightarrow {}^7F_J$ fluorescence spectra of $\text{Sm}^{2+}:\text{CaFCl}$ at 20 K and ambient pressure. The asterisks in (a), (c), and (e) represent a Sm^{3+} fluorescence line and a fluorescence line originating from a ${}^5D_1 \rightarrow {}^7F_4$ and from a ${}^5D_0 \rightarrow {}^7F_2$ transition, respectively.

2.3. Fluorescence and energy levels under pressure

All the ${}^5D_J \rightarrow {}^7F_J$ fluorescence spectra of $\text{Sm}^{2+}:\text{CaFCl}$, except the transitions ${}^5D_2 \rightarrow {}^7F_{0-3}$ and ${}^5D_1 \rightarrow {}^7F_6$, were studied at 20 K up to 8 GPa. Under pressures up to 4 GPa, only

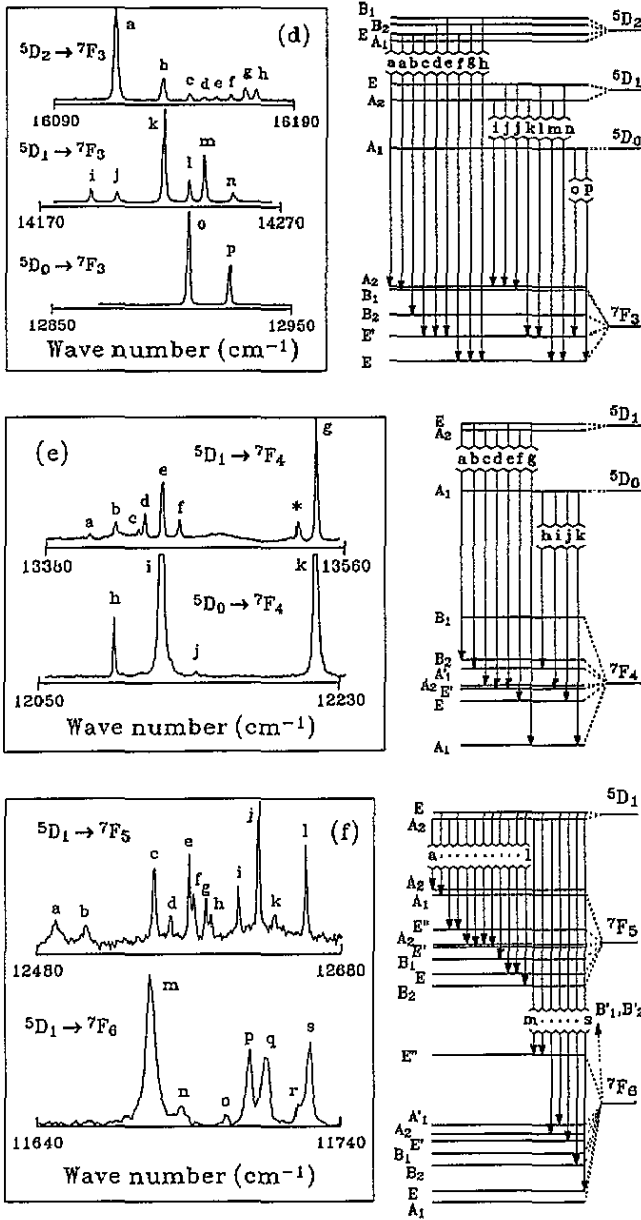


Figure 4. (Continued)

minor changes in the line widths of the fluorescence spectra were observed, however, in the pressure range from 4 GPa to 5 GPa, the line widths are greatly broadened. For example, the line width of the $5D_0 \rightarrow 7F_0$ transition increases from 1.5 cm^{-1} at 20 K and ambient pressure to 8 cm^{-1} and its line shape becomes asymmetric at 20 K and 5 GPa. This effect can be attributed to nonhydrostatic stresses. In order to eliminate such stresses, annealing the sample in the DAC was performed for four hours at $100 \text{ }^\circ\text{C}$. Subsequent measurements showed clearly reductions in line width and line asymmetry. With this procedure, the fluorescence measurements could be performed up to 8 GPa.

Table 1. Observed CF levels for $\text{Sm}^{2+}:\text{CaFCl}$ at ambient pressure.

Multiplet	CF level	Energy (cm^{-1})
${}^7\text{F}_0$	A_1	0
${}^7\text{F}_1$	E	267.2
	A_2	325.2
${}^7\text{F}_2$	B_1	789.9
	B_2	794.9
	E	802.8
${}^7\text{F}_3$	A_1	855.1
	E	1462.6
	E'	1479.4
	B_2	1492.3
${}^7\text{F}_4$	B_1	1510.0
	A_2	1510.0
	A_1	2170.9
	E	2242.0
${}^7\text{F}_5$	E'	2263.5
	A_2	2266.9
	A_1'	2291.8
	B_2	2307.3
	B_2	3057.4
	E	3077.1
	B_1	3101.9
	E'	3119.8
	A_2	3123.1
	E''	3146.3
${}^7\text{F}_6$	A_1	3202.5
	A_2'	3210.7
	E	3984.3
	B_2	3987.5
	E'	3998.6
	A_2	4000.5
${}^5\text{D}_0$	A_1'	4004.3
	E''	4026.0
${}^5\text{D}_1$	A_1	14 386.6
	A_2	15 702.4
${}^5\text{D}_2$	E	15 713.7
	E	17 627.5
	B_2	17 633.8
	B_1	17 638.4

The line shifts of the spectra are summarized in figure 5. The average shift in CaFCl is very similar to the previous results [2] for BaFCl and SrFCl ; however, there is a large difference in the pressure shifts for Sm^{3+} . Whereas the pressure shifts of the Sm^{2+} fluorescence lines amount to about $-21 \text{ cm}^{-1} \text{ GPa}^{-1}$ for ${}^5\text{D}_0$ transitions and about $-24 \text{ cm}^{-1} \text{ GPa}^{-1}$ for ${}^5\text{D}_1$ transitions, the Sm^{3+} lines shift on average with a rate of $-6 \text{ cm}^{-1} \text{ GPa}^{-1}$. This large difference allows us to distinguish very easily the fluorescence lines from Sm^{2+} and Sm^{3+} under pressure.

Finally, the observed fluorescence spectra result in an unambiguous determination of the CF levels for $\text{Sm}^{2+}:\text{CaFCl}$ under pressures up to 8 GPa, as shown in figure 6.

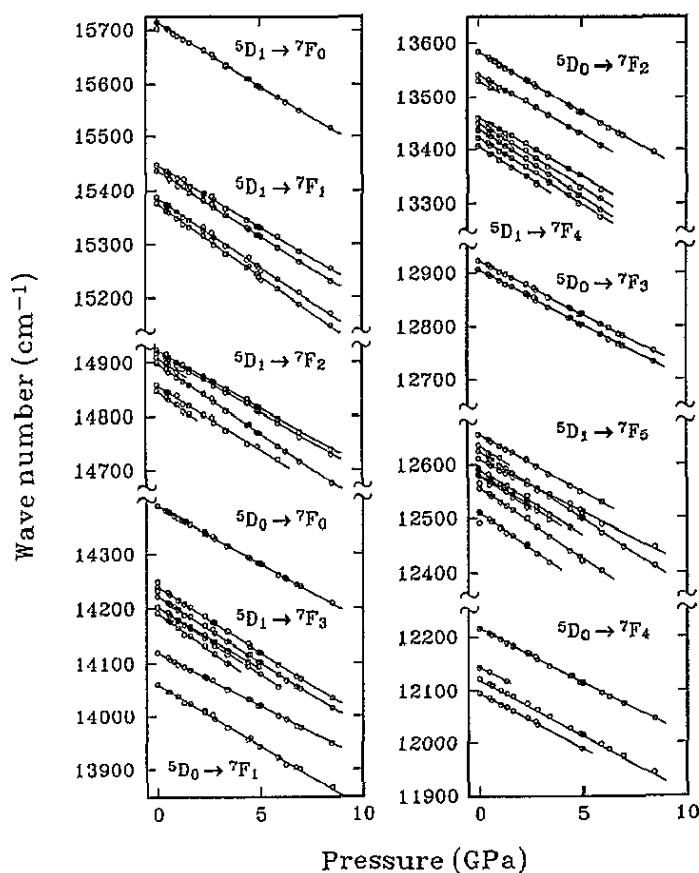


Figure 5. Line shifts for the ${}^5D_j \rightarrow {}^7F_j$ fluorescence spectra of $\text{Sm}^{2+}:\text{CaFCl}$ at 20 K and under pressure.

3. Discussion

3.1. Crystal-field analysis

The one-electron CF potential \mathcal{H}_{CF} at the Sm^{2+} site with the C_{4v} symmetry comprises five nonzero B_q^k parameters [2]: B_0^2 , B_0^4 , B_4^4 , B_0^6 , and B_4^6 .

As previously discussed [2], it is reasonable to restrict \mathcal{H}_{CF} to the 7F_j basis set in the least-squares fitting procedure of these five CF parameters. From the experimental data in table 1, the CF parameters are first obtained for ambient pressure as shown in table 2. The standard deviation σ between observed and calculated values is reduced by a factor of two when the CF-induced J mixing is taken into account. This means that the J mixing effects on Sm^{2+} in CaFCl cannot be neglected. In comparison with the results of $\text{Sm}^{2+}:\text{BaFCl}$ and $\text{Sm}^{2+}:\text{SrFCl}$ [2], the CF parameters show a very systematical variation in these three MFC hosts.

The variation of the CF parameters under pressure is determined by the same procedure. Figure 7 shows the variation of the CF parameters with the J mixing. Under pressure up to 8 GPa, the standard deviation increases gradually to $\sigma \approx 2.6 \text{ cm}^{-1}$. In general, the pressure dependence of the CF parameters for $\text{Sm}^{2+}:\text{CaFCl}$ is also qualitatively similar to

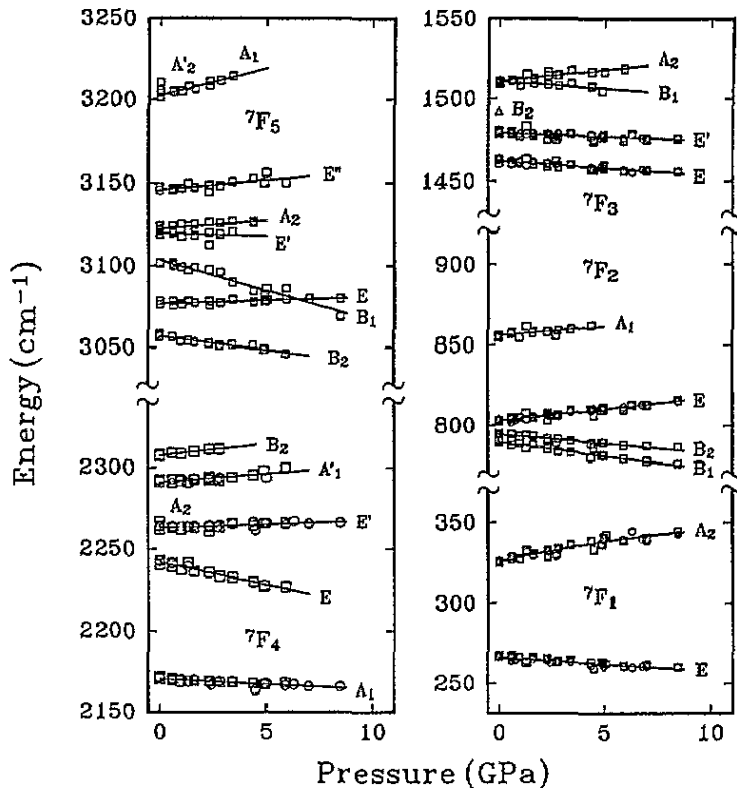


Figure 6. Effect of pressure on the CF levels of $\text{Sm}^{2+}:\text{CaFCl}$ deduced from all the line shifts in figure 5. Triangles, squares and circles denote the results from the transitions ${}^5\text{D}_2 \rightarrow {}^7\text{F}_J$, ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$, respectively.

Table 2. Crystal field parameters B_q^k (cm^{-1}) for $\text{Sm}^{2+}:\text{CaFCl}$ at ambient pressure from the 32 levels given in table 1. The data for $\text{Sm}^{2+}:\text{SrFCl}$ and $\text{Sm}^{2+}:\text{BaFCl}$ [2] are included for comparison. σ denotes the standard deviation between measured and calculated energy levels.

	$\text{Sm}^{2+}:\text{CaFCl}$		$\text{Sm}^{2+}:\text{SrFCl}$ With J mixing	$\text{Sm}^{2+}:\text{BaFCl}$ With J mixing
	Without J mixing	With J mixing		
B_0^2	211(6)	200(3)	63(2)	-93(2)
B_0^4	-284(9)	-269(4)	-220(4)	-173(4)
B_4^4	32(9)	33(4)	-17(4)	-83(3)
B_0^6	522(12)	550(6)	492(5)	398(5)
B_4^6	-288(7)	-289(3)	-231(3)	-194(3)
σ	3.0	1.5	1.5	1.4

the previous results [2] for $\text{Sm}^{2+}:\text{BaFCl}$ and $\text{Sm}^{2+}:\text{SrFCl}$. However, quantitatively, the CF parameter B_4^4 in its absolute value increases only slightly and the parameter B_4^6 stays nearly constant in the present case.

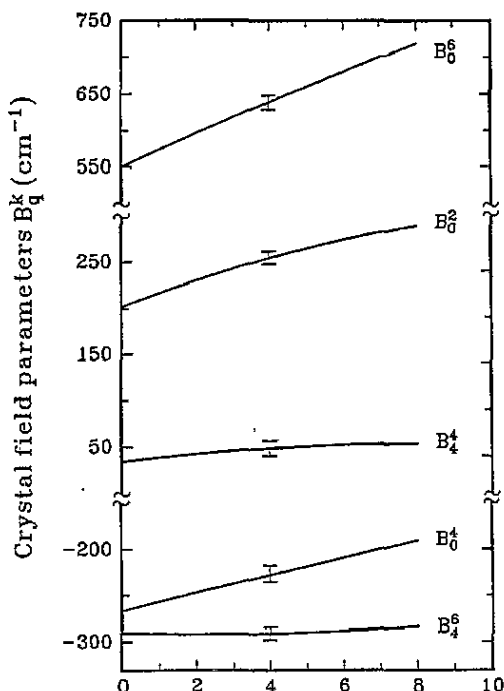


Figure 7. Variation of CF parameters for $\text{Sm}^{2+}:\text{CaFCl}$ under pressure. The statistical variance is represented by error bars.

3.2. Superposition model

The variation of CF parameters under pressure, as shown in figure 7, reflects just the different structural changes of the host crystals and the superposition model [5, 6] provides a reasonable approach to study these effects with lanthanide ions. Within this SM approach, the CF parameters B_q^k are decomposed in several parts:

$$B_q^k = \sum_L \bar{B}_k(R_L) K_{kq}(\Theta_L, \Phi_L) \quad (1)$$

where L sums over all the next-nearest ligand ions with the spherical coordinates (R_L, Θ_L, Φ_L) around the central lanthanide ion. The coordination factors $K_{kq}(\Theta_L, \Phi_L)$ are well known angular functions of the ligand ions, and the $\bar{B}_k(R_L)$, usually referred to as intrinsic (i.e. geometry-independent) CF parameters, absorb all the physical contributions from the ligands. These $\bar{B}_k(R_L)$ depend only on the ligand type and on the interionic distance R_L between the lanthanide ion and the ligand ion L in the coordination polyhedron. In the case of the electrostatic point charge model, one obtains $\bar{B}_k(R) \propto (1/R)^{k+1}$. In general, however, free power law exponents t_k are usually used with $\bar{B}_k(R) = \bar{B}_k(R_0)(R_0/R)^{t_k}$, where R_0 is a conveniently selected reference distance. It is then generally assumed that the intrinsic CF parameters $\bar{B}_k(R)$ of the SM lead to reasonable predictions of CF interactions for the given lanthanide ion with the same ligands in different hosts.

However, there are two ways to use the SM. First, the intrinsic CF parameters \bar{B}_k can be extracted from experimentally determined CF parameters by use of equation (1), when experimental data, for instance from x-ray measurements, are available for the ligand

positions. On the other hand, one can derive information on the local structure, i.e. ligand positions around lanthanide ions in crystals, when systematics in the intrinsic CF parameters are known.

In the MFCl host crystals, nine ligand ions surround each Sm^{2+} ion, whereby four F and four Cl ions are equivalent by symmetry and one extra Cl ion labelled as Cl' is located on the fourfold symmetry axis on top of the central Sm^{2+} ion. The corresponding coordinates are denoted by (R_F, Θ_F, Φ_F) , $(R_{\text{Cl}}, \Theta_{\text{Cl}}, \Phi_{\text{Cl}})$, and $(R_{\text{Cl}'}, \Theta_{\text{Cl}'}, \Phi_{\text{Cl}'})$ with $\Phi_F = (45^\circ, 135^\circ, 225^\circ, 315^\circ)$, $\Phi_{\text{Cl}} = (0^\circ, 90^\circ, 180^\circ, 270^\circ)$, and $\Theta_{\text{Cl}'} = 0^\circ$. The contributions from these nine ligands to the CF parameters B_0^k and B_4^k ($k = 4$ and 6) of Sm^{2+} in MFCl are given within the SM by

$$\begin{aligned} B_0^k &= \bar{B}_k(R_{\text{Cl}})\bar{K}_{k0}^{\text{Cl}} + \bar{B}_k(R_F)K_{k0}^{\text{F}} \\ B_4^k &= \bar{B}_k(R_{\text{Cl}})K_{k4}^{\text{Cl}} + \bar{B}_k(R_F)K_{k4}^{\text{F}} \end{aligned} \quad (2)$$

where $\bar{K}_{k0}^{\text{Cl}} = K_{k0}^{\text{Cl}} + (R_{\text{Cl}}/R_{\text{Cl}'})^{t_k^{\text{Cl}}}$ takes into account the fact that the four equivalent Cl ions at the distance R_{Cl} contribute the term K_{k0}^{Cl} and the one extra Cl' ion at the different distance $R_{\text{Cl}'}$ contributes with the different strength $\bar{B}(R_{\text{Cl}'}) = \bar{B}(R_{\text{Cl}})(R_{\text{Cl}}/R_{\text{Cl}'})^{t_k^{\text{Cl}}}$. The collective coordination factors K_{kq}^{Cl} and K_{kq}^{F} are only functions of the angles Θ_{Cl} and Θ_F , respectively, because the special values for Φ_{Cl} and Φ_F affect only the sign of K_{kq} ; these are rewritten in terms of associated Legendre functions $P_k^q(\Theta)$ as

$$K_{40}(\Theta) = 4P_4^0(\Theta) \quad K_{44}(\Theta) = \pm(\sqrt{70}/425)P_4^4(\Theta)$$

$$K_{60}(\Theta) = 4P_6^0(\Theta) \quad K_{64}(\Theta) = \pm(\sqrt{14}/1260)P_6^4(\Theta).$$

where the + sign refers to the values for Cl ions, due to the value for $\cos 4\Phi_{\text{Cl}} = 1$, and the - sign must be used for F ions, due to the different value $\cos 4\Phi_F = -1$.

In the previous study [2] on $\text{Sm}^{2+}:\text{BaFCl}$ and $\text{Sm}^{2+}:\text{SrFCl}$, the parameters \bar{B}_k and t_k ($k = 4$ and 6) had been derived for both $\text{Sm}^{2+}-\text{Cl}^-$ and $\text{Sm}^{2+}-\text{F}^-$ ion pairs, respectively, as $\bar{B}_4(R_{\text{Cl}}^0) = 124(14) \text{ cm}^{-1}$, $t_4^{\text{Cl}} = 14(4)$, $\bar{B}_6(R_{\text{Cl}}^0) = 152(16) \text{ cm}^{-1}$, $t_6^{\text{Cl}} = 10(3)$, $\bar{B}_4(R_{\text{F}}^0) = 245(25) \text{ cm}^{-1}$, $t_4^{\text{F}} = 5.8(1.5)$, $\bar{B}_6(R_{\text{F}}^0) = 172(18) \text{ cm}^{-1}$, and $t_6^{\text{F}} = 4.6(1.1)$ with the use of the reference distances $R_{\text{Cl}}^0 = 311.4 \text{ pm}$ and $R_{\text{F}}^0 = 249.6 \text{ pm}$. If one transfers these results to $\text{Sm}^{2+}:\text{CaFCl}$, the local structure around Sm^{2+} in CaFCl can be deduced with the use of equation (2), since all the distance dependences are known from the previous results.

In fact, the local structure of the substitutional Sm^{2+} ion is best described by four local structural parameters as defined in figure 8, where two coordination cell parameters a^{loc} and c^{loc} and two local position parameters z_{Sm} and $z_{\text{Cl}}^{\text{loc}}$ are used to determine the five local parameters $R_{\text{Cl}}^{\text{loc}}$, $R_{\text{Cl}'}^{\text{loc}}$, $R_{\text{F}}^{\text{loc}}$, $\Theta_{\text{Cl}}^{\text{loc}}$, and $\Theta_{\text{F}}^{\text{loc}}$, which enter into equation (2). The intrinsic CF parameters for the $\text{Sm}^{2+}-\text{Cl}^-$ and $\text{Sm}^{2+}-\text{F}^-$ ion pairs and the experimental CF parameters for $\text{Sm}^{2+}:\text{CaFCl}$ lead with equation (2) to four independent equations, which determine these four local structural parameters at each pressure with the following results.

(i) The effect of pressure on the local cell parameters a^{loc} and c^{loc} is very similar to the effect on the host lattice parameters a and c , as shown in figure 9. The differences $\Delta a = a^{\text{loc}} - a$ and $\Delta c = c^{\text{loc}} - c$ represent the local distortions in the CaFCl host around substitutional Sm^{2+} ions due to their considerably larger size in comparison with Ca^{2+} . These local distortions amount to $\Delta a = 12(2) \text{ pm}$ and $\Delta c = -16(3) \text{ pm}$ or $3.0(5)\%$ and $-2.3(4)\%$ at ambient pressure. The opposite signs of Δa and Δc fit very well to the structural systematics of the PbFCl-type MYX compounds including MFX, MHX, and MOX [7].

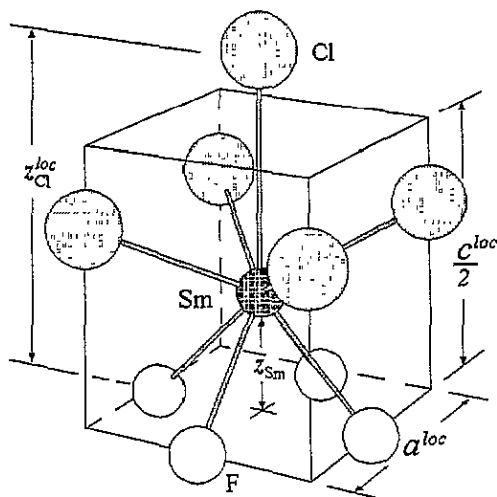
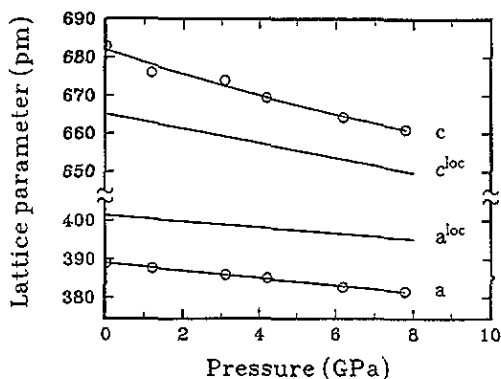


Figure 8. Local unit cell.

Figure 9. Comparison of the host lattice parameters a and c for CaFCl from [7] with the present values for the local cell parameters a^{loc} and c^{loc} .

(2) The Sm^{2+} position parameter in CaFCl is $z_{\text{Sm}} = 0.197(2)$ at ambient pressure, which is close to the value $z_{\text{Ca}} = 0.196(2)$ for CaFCl at ambient conditions [8]. A single-crystal x-ray study on BaFCl under pressures up to 6.5 GPa indicates that z_{Ba} increases slightly with a rate of $9.2(8) \times 10^{-4} \text{ GPa}^{-1}$, whereas the present determination results in a nearly constant value for z_{Sm} in CaFCl under pressure.

(3) The value $z_{\text{Cl}}^{\text{loc}} = 0.658(2)$ for Sm^{2+} in CaFCl at ambient pressure deviates only slightly from the Cl parameter $z_{\text{Cl}} = 0.643(2)$ of the CaFCl host [8], and agrees well with the average value $z_{\text{X}} = 0.647(14)$ given in [7] for all the MYX compounds, where an almost constant value for z_{X} was noticed, in other words, a value independent of cation or anion sizes. Moreover, the present calculation gives a negligible decrease in $z_{\text{Cl}}^{\text{loc}}$ under pressure in close agreement with the previous high-pressure results for BaFCl [9] and PbFCl [10].

Of course, instead of these four local structural parameters, the local distances ($R_{\text{Cl}}^{\text{loc}}$ and $R_{\text{F}}^{\text{loc}}$) and angles ($\Theta_{\text{Cl}}^{\text{loc}}$ and $\Theta_{\text{F}}^{\text{loc}}$) could also be used to describe the local distortions around Sm^{2+} in CaFCl , and the changes $\Delta R_{\text{Cl}} = 3.4(5) \text{ pm}$ and $\Delta R_{\text{F}} = 3.5(5) \text{ pm}$ correspond then just to about 10% of the difference in the ionic radii, in close agreement with the previous

results for $\text{Sm}^{2+}:\text{BaFCl}$, where the distortion amounts to 12% of the difference in the ionic radii between Sm^{2+} and Ba^{2+} .

4. Conclusions

The present results on $\text{Sm}^{2+}:\text{CaFCl}$ under pressure demonstrate, for the first time, that calibrated intrinsic CF parameters $\bar{B}_k(R)$ can be used within the SM to determine accurately local distortions around fluorescent lanthanide ions in different host lattices just by high-pressure fluorescence studies.

Acknowledgments

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