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Effects of electron correlation in crystal-field splittings of Sm^{2+} in *M*FCl-type hosts

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Effects of pressure on the crystal-field splittings of the $^5D_1$ and $^7F_1$ multiplets were studied for Sm^{2+} in *M*FCl (M=Ba, Sr, and Ca). A comparison with experimental data from the literature for Eu^{3+} in different compounds at ambient pressure and partly under pressure shows that the splittings of $^5D_1$ and $^7F_1$ are successfully explained in the case of Eu^{3+} by the spin-correlated crystal-field (SCCF) model, when a constant SCCF parameter $c_2 = -0.007(3)$ is used. For Sm^{2+}, however, the experimental results cannot be described by the same SCCF model. In fact, the pressure dependence of the splittings in the two multiplets $^5D_1$ and $^7F_1$ for Sm^{2+}:BaFCl to Sm^{2+}:CaFCl deviates extremely not only from the predictions of the conventional crystal-field models but also from the SCCF model, but these results are qualitatively explained when a significant configuration interaction between the $4f^6$ and $4f^5 5d^1$ configurations is taken into account. The present study shows that this $4f$-$5d$ configuration interaction results in very important contributions to correlation crystal fields for Sm^{2+} due to the close energetic proximity of these two configurations.

Introduction. Although conventional (one-electron) crystal-field (CF) models have been applied very successfully to describe crystal-field interactions of f^n-electron systems in solids, anomalous crystal-field splittings of certain multiplets (for example, $^2H_{11/2}$ of Nd^{3+}, $^3K_8$ of Ho^{3+}, ^5D_J of Eu^{3+}, etc.) are not well fitted within these approximations and the breakdown of the conventional CF models is usually ascribed to correlation effects between the f electrons in these cases.

The correlation effects are described by means of effective (two-electron) crystal-field operators.[1] The main problem of correlation crystal fields (CCF's) results from the introduction of a very large number of new parameters, and the physical meaning of these parameters is not well understood. The large number of parameters can be reduced by the use of simplified CCF models, as, for instance, the so-called spin-correlated crystal-field (SCCF) model.[2] This approach is based on different wave functions for the spin-up and spin-down electrons, which doubles only the number of CF parameters.

On the other hand, a suitable subset or a special combination of parameters can be selected on the basis of experimental data for a specific system, where correlation effects are observed. For example, in an orthogonal CCF the parameters G^4_{10AQ} for Nd^{3+} give important contributions to the $^2H_{11/2}$ multiplet,[3] and the first observation of pressure-induced variations in CCF effects on Nd^{3+}:$LaCl_3$ has shown that the distance dependence of the CCF parameters differs very much from the variations of the conventional CF parameters.[4]

For Eu^{3+} with a ground $4f^6$-configuration, the problems occurring with the ^5D_J-splittings in the conventional CF fits have not yet been treated within the CCF. Although some CF fits for Eu^{3+} in different host crystals have been improved by the use of arbitrarily modified matrix elements,[8] the physical origin for this improvement is not understood.

Since the electronic configuration of Sm^{2+} is isoelectronic to Eu^{3+}, Sm^{2+} ions in different *M*FCl host crystals are studied here at ambient and elevated pressure just as another test case for CCF effects in this $4f^6$ configuration.

Experiment. Single crystals of *M*FCl with a concentration of 0.1 mol % Sm^{2+} were grown for the present study by the Bridgman method in the materials laboratory of the University Paderborn. A small diamond anvil cell[5] (DAC) was used to generate pressures up to 8 GPa at temperatures down to about 20 K with a closed cycle refrigerator (model 21SC cryodyne cryocooler). Fluorescence spectra were excited by an argon ion laser and measured with a double grating spectrometer (Spex model 14018).

Results and discussion. Typical fluorescence spectra of Sm^{2+}: *M*FCl in the range of the $^5D_1 \rightarrow {}^7F_1$ transition are shown in Fig. 1 for ambient pressure and 20 K. Four fluorescence lines are observed in this case. The multiplet with $J=1$ splits into two crystal-field levels A_2 and E, according to the site symmetry C_{4v} for Sm^{2+} at M site in the *M*FCl host lattice. All of the symmetry-allowed transitions for $^5D_1 \rightarrow {}^7F_1$ are easily assigned (see Fig. 1). At ambient pressure, the fluorescence lines show a large red shift from BaFCl to CaFCl, but the shifts of the lines a and b are much larger than for c and d. This indicates that the energy positions of the two crystal-field levels $^7F_1(A_2)$ and $^7F_1(E)$ interchange between BaFCl and SrFCl.

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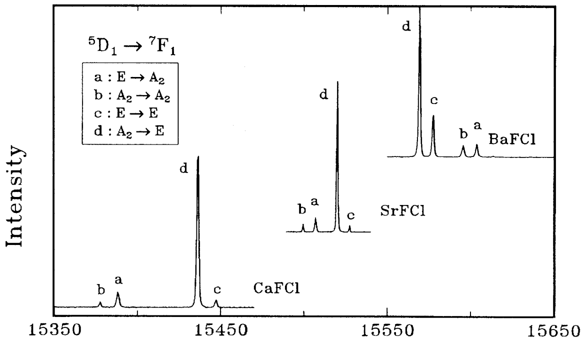

FIG. 1. $^5D_1 \rightarrow {}^7F_1$ fluorescence spectra of Sm^{2+}: *M*FCl at ambient pressure and 20 K.

The effect of pressure on the line positions was studied for all the samples typically up to 8 GPa. Figure 2 represents spectra for the $^5D_1 \rightarrow {}^7F_1$ transition of Sm^{2+}:BaFCl at different pressures and 20 K. The pressure-induced red shifts for the lines *a* and *b* are again much larger than for *c* and *d*. The crystal-field levels A_2 and E for both $^5D_1$ and $^7F_1$ are easily derived from the observed spectra and Fig. 3 shows just the pressure dependences of the relative splittings of $^5D_1(A_2)$ and $^5D_1(E)$ with respect to the $^5D_1$-multiplet centroid. The shift of the $^5D_1$-multiplet centroid under pressure is $-24(1)$ cm^{-1}/GPa for Sm^{2+} in these three host crystals. The pressure dependences of the two crystal-field levels of $^7F_1$ are shown in Fig. 4, whereby the energy is measured with respect to the $^7F_0$ ground multiplet. A crossing of $^7F_1(A_2)$ and $^7F_1(E)$ in the case of Sm^{2+}:BaFCl is seen at about 4 GPa.

For comparison with the present results on Sm^{2+}: *M*FCl, the experimental literature data for Eu^{3+} in different host crystals are listed in Table I.

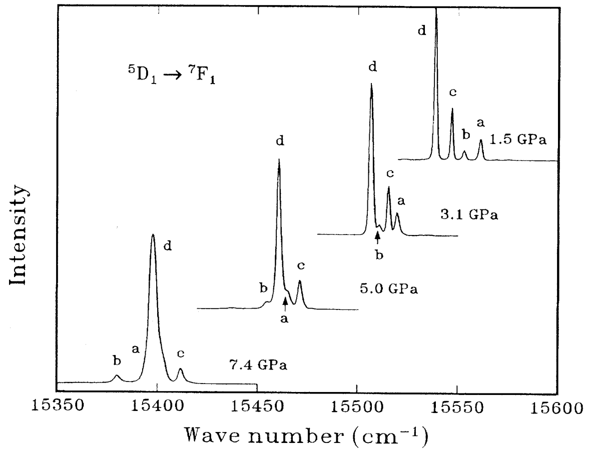

FIG. 2. Typical $^5D_1 \rightarrow {}^7F_1$ fluorescence spectra of Sm^{2+}:BaFCl at 20 K and different pressures. The assignment of the fluorescence lines is the same as in Fig. 1.

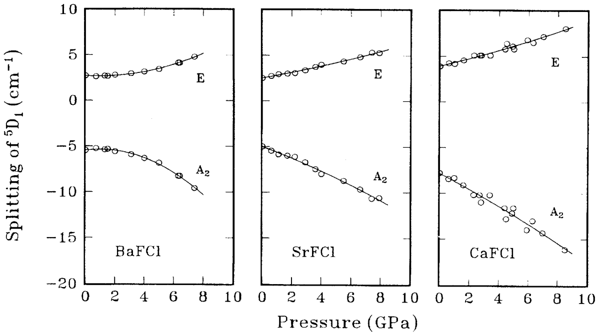

FIG. 3. Pressure dependences of the crystal-field splittings for the $^5D_1$ multiplet with respect to the multiplet centriod.

In the conventional CF approach, the splittings for both $^5D_1$ and $^7F_1$ multiplets should be similar and the splitting ratio $\mathscr{R}$ can be written as

$$\mathscr{R}=\frac{\Delta(^5D_1)}{\Delta(^7F_1)}=\frac{\begin{Bmatrix}1&1&2\\2&2&2\end{Bmatrix}\langle ^5D||U^2||^5D\rangle}{\begin{Bmatrix}1&1&2\\3&3&3\end{Bmatrix}\langle ^7F||U^2||^7F\rangle}\,.$$

Thereby, the splittings Δ are defined as an energy separation between the twofold degenerate ($M_J=\pm 1$) and the nondegenerate ($M_J=0$) levels of the $^5D_1$ and $^7F_1$ multiplets, respectively. For the ratio $\mathscr{R}$ one can easily obtain $\mathscr{R}=0.298$ (cf. Judd[7]), independent of the crystal-field strength and therefore also independent of the host crystals. To compare this theoretical result with the experimental data, the variation of $\Delta(^5D_1)$ against $\Delta(^7F_1)$ is shown in Fig. 5. The dashed line in this figure corresponds to the conventional CF result, which shows a discrepancy between this theoretical prediction and the experimental results. Thus either the second-order crystal-field effect—*J* mixing or CCF effects have to be taken into account. Since the *J* mixing does not improve the results in the present case,[6] this discrepancy must be regarded as a direct indication for CCF effects.

It can be noted that this discrepancy was largely eliminated by Moune[8] using just an empirical scaling of one reduced matrix element $\langle ^5D(3)||U^2||^5D(3)\rangle$. This purely empirical approach has been applied to Eu^{3+} in 15 different host crystals, leading to a modified effective $\mathscr{R}=0.174$. However, it was not clear which physical mechanisms should be responsible for this reduction.

Besides this empirical scaling, the SCCF model was ap-

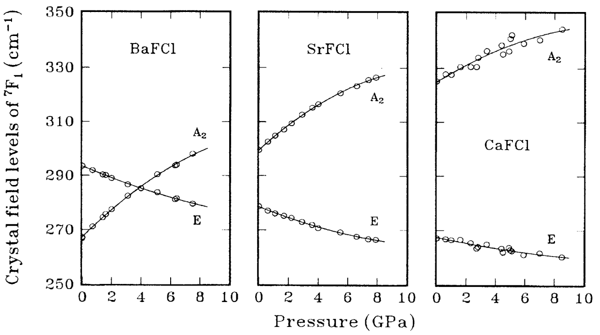

FIG. 4. Variation of the crystal-field levels for the $^7F_1$ multiplet under pressure.

TABLE I. Experimental data of the crystal-field levels of the $^5D_1$ and $^7F_1$ multiplets for Eu^{3+} in various host crystals at ambient pressure.

		$^5D_1$		$^7F_1$		
Host lattice	Symmetry	$m=\pm1$	$m=0$	$m=\pm1$	$m=0$	Ref.
LaOCl	C_{4v}	19060	18985	479	189	9
LaOBr	C_{4v}	19089	19006	508	162	10
LaOI	C_{4v}	19073	18992	505	167	10
GdOCl	C_{4v}	18992	18944	452	234	9
GdOBr	C_{4v}	19003	18942	464	213	10
YOCl	C_{4v}	18976	18934	438	246	9
YOBr	C_{4v}	18984	18931	451	226	10
KY_3F_{10}	C_{4v}	19039	19007	411	278	11
$LiYF_4$	S_4	19019	19040	334	430	12
$Na_5Eu(MoO_4)_4$	S_4	18957	18975	346	406	13
$Na_5Eu(WO_4)_4$	S_4	18961	18977	347	399	13
EuES(RT)	D_{3h}	19024.6	19028.5	361.4	394.1	14
EuES(4K)	D_{3h}	19013.9	19018.7	356.5	400.6	15
$LaCl_3$	D_{3h}	19025.6	19034.4	355.1	405.3	16
$GdCl_3$	D_{3h}	19006.8	19018.3	352.6	414.7	17
$Eu(HO)_3$	C_{3h}	18977.7	18996.1	335.0	435.8	18
$LaAlO_3$	D_3	18990	18975	380	314	19
La_2O_2S	C_{3v}	18939.6	18946.8	350.8	376.9	20
Gd_2O_2S	C_{3v}	18906.4	18914.0	348.9	381.5	20
Y_2O_2S	C_{3v}	18894.0	18901.7	346.9	384.5	20
Lu_2O_2S	C_{3v}	18879.8	18886.2	346.1	383.8	20
BaF_2	C_{3v}	19057	19070	327	392	21
YPO_4	D_{2d}	18964.5	18986.1	339.4	435.6	22
YVO_4	D_{2d}	18941	18932	375.6	333.7	23

plied in the present study to disclose the possible origin for this discrepancy. From the SCCF model,[2] the splitting ratio is found to be

$$\mathscr{R}=\tfrac{11}{45}+\tfrac{79}{90}c_2,$$

thereby c_2 is defined as a ratio between the SCCF parameters b_q^2 and the conventional CF parameters B_q^2. A common value of $-0.007(3)$ for c_2 is found for all Eu^{3+} samples considered in Table I. This SCCF result points in the same direction, which is also expected theoretically,[24] and is shown by the solid line in Fig. 5 which gives a reasonable description for all the Eu^{3+} data at ambient pressure.

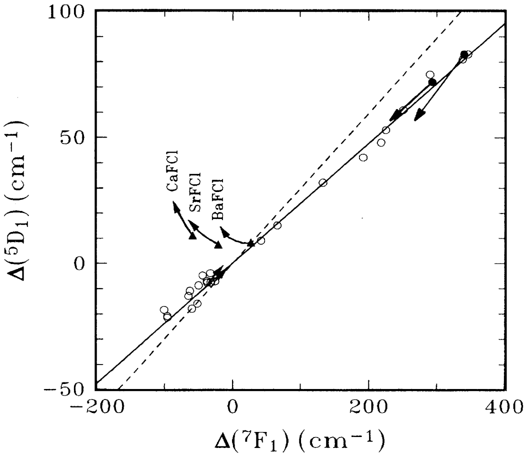

FIG. 5. Variation of the crystal-field splittings $\Delta(^5D_1)$ vs $\Delta(^7F_1)$ for Eu^{3+} (open circles, the data used from Table I) as well as for Sm^{2+} (closed triangles) at ambient pressure. Arrows represent variations under pressure. The dashed and solid lines denote the theoretical CF and SCCF results, respectively (see text).

As illustrated in Fig. 5, also the pressure dependences for Eu^{3+}:LaOCl (up to 13 GPa),[25] Eu^{3+}:LaOBr (up to 13 GPa),[26] Eu^{3+}:La_2O_2S (up to 10 GPa),[27] and Eu^{3+}:Y_2O_2S (up to 10 GPa)[28] are well described by this SCCF model. However for Sm^{2+} in *M*FCl, the situation is quite different. Whereas $\mathscr{R}$ = 0.31 for Sm^{2+}:BaFCl at ambient pressure agrees still with the conventional CF result, the pressure dependences deviate extremely in all the Sm^{2+} cases from the predictions of the SCCF model.

Thus, one is left with the question, why can the SCCF model describe the experimental results of Eu^{3+}, but not in the case of Sm^{2+}, when both Sm^{2+} and Eu^{3+} have the same $4f$ configuration?

At first, one can think of two possibilities: (1) In contrast to Eu^{3+}, c_2 for Sm^{2+} could be considered as a variable parameter within the context of the SCCF model, or (2) the SCCF model breaks down in the case of Sm^{2+} for another reason.

A variable parameter c_2 implies that the distance dependences of the CCF parameters should be different from those of the conventional CF parameters. Concerning this point, a recent study on the CCF effects of Nd^{3+}:$LaCl_3$ under pressure has indicated that the distance dependence for the CCF interactions is much larger than for the conventional CF interactions ($k=4$).[4] Thus one could assume that also in the case of Sm^{2+} the SCCF parameter b_0^2 could vary with a different distance dependence in comparison with the CF parameter B_0^2. However, in the frame of the SCCF model this assumption leads to an unreasonable result. When the splitting of $^7F_1$ goes through zero, the parameter c_2 would have to be infinite, so that it finally loses its physical meaning. This indicates directly that the SCCF model alone cannot explain these anomalies of Sm^{2+}.

In any case, the SCCF represents only a special form of the general CCF model. According to the relationship between the SCCF and the so-called "orthogonal" CCF, the SCCF parameter b_0^2 is expressed as a linear combination of two CCF parameters G_{20}^2 and G_{30}^2.[29] The CCF calculations for the system Pr^{3+}- Cl^- (Ref. 30) show that also some of the other CCF parameters are particularly large, notably G_4^2, G_8^2, G_9^2, and G_{10}^2, and they are not absorbed in the SCCF model. Thus the general CCF must be applied in the case of Sm^{2+}.

Since the main difference between Sm^{2+} and Eu^{3+} is a small compression of the energy scale due to smaller Coulomb and spin-orbit interactions caused by the smaller effective nuclear charge of Sm^{2+},[31] the $4f^6$ configuration for Eu^{3+} is relatively isolated and the first excited $4f^55d^1$ configuration starts at about 50 000 cm^{-1} above the ground multiplet $^7F_0$. On the other hand, the $4f^55d^1$ configuration of Sm^{2+} in BaFCl is observed in absorption and excitation measurements[32,33] only at about 20 000 cm^{-1}. Therefore, one may assume that the deviations from the SCCF are caused in the case of Sm^{2+} by the much stronger configuration interactions between $4f^55d^1$ and $4f^6$ in comparison with Eu^{3+}.

A direct study on the contribution of the configuration interaction between $4f^2$ and $4f^15d^1$ of Pr^{3+} to the crystal-field splittings has been reported recently.[34] The well-known discrepancy in the $^1D_2$ multiplet, arising from CCF effects, was thereby eliminated by taking into account the $4f$-$5d$ configuration interaction. From this observation one must expect that the $4f$-$5d$ configuration interaction should be even considerably stronger for Sm^{2+} due to the close spacing between the $4f^6$ and $4f^55d^1$-configurations in this case.

Therefore the absorption spectrum of Sm^{2+}:SrFCl was finally also measured in the present study at 20 K and ambient pressure and it was found that the $5d$ configuration of Sm^{2+}:SrFCl is about 1000 cm^{-1} lower in comparison to Sm^{2+}:BaFCl. Also the pressure dependences for Sm^{2+}:SrF_2 (Ref. 35) and a quenching in fluorescence intensities for Sm^{2+}:*M*FCl with increasing pressures show larger pressure-induced shifts of $5d \rightarrow 4f$ vs $4f \rightarrow 4f$. Thus, it must be concluded that the $4f$-$5d$ configuration interaction results in significant contributions to the CCF effects for Sm^{2+} and these results may stimulate further theoretical considerations on CCF effects in the $4f^6$-configuration.

Conclusions. The present analysis of CF levels for Eu^{3+} in different host crystals illustrates that the splitting ratio $\mathscr{R}$ for $^5D_1$ and $^7F_1$ gives a direct measure of the CCF effect within the $4f^6$ configuration and the simplifying SCCF model works reasonably for Eu^{3+} systems. This SCCF model fails, however, in the case of Sm^{2+}, where the $4f^55d^1$ configuration leads to significant modifications for the $4f^6$ CCF and to a breakdown of the simpler SCCF model.

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