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Pressure-induced changes in Cr\textsuperscript{3+}-doped elpasolites and LiCaAlF\textsubscript{6}: Interpretation of macroscopic data

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In the research of pressure effects on Cr\textsuperscript{3+}-doped insulating lattices, it is crucial to understand the dependence of the 10D\textsubscript{q} parameter on the sample volume, V. This problem is explored in the present work through \textit{ab initio} calculations on Cr\textsuperscript{3+}-doped K\textsubscript{2}NaScF\textsubscript{6}, C\textsubscript{8}S\textsubscript{2}NaYCl\textsubscript{6}, and C\textsubscript{8}S\textsubscript{2}NaYBr\textsubscript{6} elpasolite lattices as a function of pressure in the 0–5 GPa range. From the calculated values of the lattice parameter and the Cr\textsuperscript{3+}-X\textsuperscript{−} (X=F, Cl, and Br) distance, it is found that for each of the investigated lattices, pressure modifies the energy of electronic transitions related to the Cr\textsuperscript{3+} emission.\textsuperscript{5,6} Moreover, in the case of halide host lattices doped with Cr\textsuperscript{3+} ions, pressure can change the nature of the first excited state responsible for the luminescence. This spin crossover transition produces a strong variation in the emission pattern going from a broad band to a sharp one.\textsuperscript{7–10}

Among the host lattices used for incorporating Cr\textsuperscript{3+} impurities, a great deal of work has been carried out on those involving a trivalent cation such as Al\textsubscript{2}O\textsubscript{3}, K\textsubscript{2}NaScF\textsubscript{6}, K\textsubscript{2}NaYCl\textsubscript{6}, or LiCaAlF\textsubscript{6}. Indeed in these cases, the Cr\textsuperscript{3+} impurity enters the trivalent site thus giving rise to a center without any close charge compensation, a situation which is thus markedly different from that appearing in systems such as KMF\textsubscript{3}:Cr\textsuperscript{3+} or K\textsubscript{2}MF\textsubscript{4}:Cr\textsuperscript{3+} (M=Mg and Zn) where different centers are simultaneously observed.\textsuperscript{8,9,20}

When a hydrostatic pressure, P, is applied on a halide lattice doped with Cr\textsuperscript{3+} it is crucial to look into the variations induced on the cubic-field splitting parameter, 10D\textsubscript{q}. Indeed this parameter alone governs the position of the first spin allowed transition \textit{A}\textsubscript{2} → \textit{E} in octahedral symmetry and, in particular, its separation with respect to the sharp \textit{A}\textsubscript{2} → \textit{E} transition as the latter is much less sensitive to an applied pressure.\textsuperscript{5,6,11} Experimental results obtained on pure insulator materials such as NiO or MnO under pressure reveal that 10D\textsubscript{q} is related to the macroscopic sample volume, V, through the law,

\[
\frac{10Dq}{10Dq_0} = \left(\frac{V_0}{V}\right)^{m/3}.
\]

Here \(V_0\) and \(10Dq_0\) refer to the values at zero pressure while the exponent \(m\) is found to be equal to 5. A similar law has been derived for ruby under pressure\textsuperscript{1} obtaining \(m=4.5\). Values of the exponent \(m\) around 5 have also been measured for Al\textsubscript{2}O\textsubscript{3} doped with trivalent cations\textsuperscript{23} such as Ti\textsuperscript{3+}, V\textsuperscript{3+}, or Ni\textsuperscript{3+}.

From a microscopic standpoint when an impurity, \(M^+\), enters an insulating lattice its valence electrons are usually confined in the \(MX_n^−\) complex formed with the \(N\) nearest \(X^−\) anions.\textsuperscript{24} Along this line, it should be noticed that according to Kohn, the localization of electrons is the fingerprint of every insulating material.\textsuperscript{25,26} Bearing in mind these considerations, it turns out that 10D\textsubscript{q} for an octahedral \(MX_6^−\) complex macroscopically depends on the \(M-X\) distance, \(R\). The law describing the \(R\) dependence of 10D\textsubscript{q} derived from theoretical calculations is found to be\textsuperscript{24–28}

\[
\frac{10Dq}{10Dq_0} = \left(\frac{R_0}{R}\right)^n,
\]

where the \(n\) exponent is usually found to lie in the 4–6 region.\textsuperscript{24} The microscopic origin of this strong dependence of 10D\textsubscript{q} on \(R\) has previously been discussed.\textsuperscript{24,29} The link between Eqs. (1) and (2) is easily made for NiO or MnO compounds exhibiting a NaCl crystal structure. Indeed in this simple lattice structure the cell volume, \(v_0\), and thus the sample volume, \(V\), are \textit{necessarily} proportional to \(R^3\) thus implying \(m=n\).

However, recent measurements carried out on LiCaAlF\textsubscript{6}:Cr\textsuperscript{3+} reveal\textsuperscript{10} that the macroscopic exponent \(m\) is not close to 5 but only equal to 2.3 a result which is thus seemingly surprising when compared to the figures measured.
Cs$_2$NaYBr$_6$ is varied by a hydrostatic pressure we do not reflect that the simple cubic power relation between $R$ and the cell volume, $a$, no longer holds. In fact, in the colquiriite-type LiCaAlF$_6$ structure the CrF$_6^{3-}$ complex (formed under $\text{Al}^{3+}\rightarrow\text{Cr}^{3+}$ substitution) is embedded in a softer region involving monovalent and divalent cations. A similar situation holds for cubic elpasolite lattices such as K$_2$NaScF$_6$, Cs$_2$NaYCl$_6$, or Cs$_2$NaYBr$_6$ varied by a hydrostatic pressure we do not know, a priori, how this change will modify the microscopic volume of the hard CrX$_6^{3-}$ unit (X=F, Cl, and Br) contained in it. 

Bearing in mind this analysis, a quantitative interpretation of the experimental dependence of 10$^3d_R$ on the macroscopic volume, $V$, requires one to determine the actual relationship between the cell volume and $R$ for any applied pressure. This work is aimed at building this bridge by means of ab initio calculations. As, at variance with colquiriite LiCaAlF$_6$, elpasolites such as K$_2$NaScF$_6$, Cs$_2$NaYCl$_6$, or Cs$_2$NaYBr$_6$ are cubic, we have first looked into the pressure dependence of this goal, we report here the calculated pressure dependence for this simpler type of lattice. In order to properly achieve this goal, we report here the calculated pressure dependence of 10$^3d_R$ for Cr$_{3+}$-doped K$_2$NaScF$_6$, Cs$_2$NaYBr$_6$, and Cs$_2$NaYCl$_6$ lattices involving different halide anions. Data corresponding to the first two systems have been calculated for the present work while results for Cs$_2$NaYCl$_6$:Cr$_{3+}$ have been derived from the analysis of data conveyed in a previous study.

Seeking to obtain reliable values of $a$ and $R$ parameters as a function of $P$, we have performed both periodic and cluster calculations following a method which has previously been tested. Periodic calculations have been performed by means of plane-wave calculations using pseudopotentials under the framework of the density-functional theory. The

for Al$_2$O$_3$:M$^{3+}$ ($M=\text{Cr, Ti, V, and Ni}$), NiO, or MnO under hydrostatic pressures. Nevertheless, considering the crystal structure of LiCaAlF$_6$ (Fig. 1) the anomalous value of the exponent $m$ measured for LiCaAlF$_6$:Cr$^{3+}$ might simply reflect that the simple cubic power relation between $R$ and the cell volume, $a$, no longer holds. In fact, in the colquiriite-type LiCaAlF$_6$ structure the CrF$_6^{3-}$ complex (formed under $\text{Al}^{3+}\rightarrow\text{Cr}^{3+}$ substitution) is embedded in a softer region involving monovalent and divalent cations. A similar situation holds for cubic elpasolite lattices such as K$_2$NaScF$_6$, Cs$_2$NaYCl$_6$, or Cs$_2$NaYBr$_6$ and metal-ligand distance, $R$, in Cr$^{3+}$-doped K$_2$NaScF$_6$, upon applied pressure. (b) Relative variation in the lattice constant with respect to the metal-ligand distance in K$_2$NaScF$_6$:Cr$^{3+}$. Perdew-Burke-Ernzehoff exchange-correlation functional was employed in combination with the Fritz-Haber institute library’s pseudopotentials, a 2×2×2 reciprocal-space sampling mesh and a plane-wave kinetic energy cutoff of 40 hartree. The ABINIT code version 5.4.4 was used throughout these calculations. In particular, we have performed geometry optimizations for several values of the pressure in the range from 0 to 5 GPa, keeping the symmetry of the lattice. At each value of the external pressure, both the lattice parameter, $a$, and the $R$ parameter, characteristic of the elpasolite structure [Fig. 1(b)], have been derived. In a second step, the geometry of Cr$_{X_6}M_{X_6}^{11+}$ (X=F, Cl, Br, and I; $M=\text{Cs and K}$) clusters has been optimized to obtain the local geometry around the Cr$^{3+}$ impurity in the three K$_2$NaScF$_6$, Cs$_2$NaYCl$_6$, and Cs$_2$NaYBr$_6$ cubic elpasolites. In this case, the calculations were performed using the Becke-Perdew exchange-correlation functional and high-quality basis sets of triple-$\zeta$ plus polarization type formed of localized Slater-type functions as implemented in the 2008 and 2009 version of the ADF code. Additional data on the method of calculation can be found in Ref. 31.

Obtained results on the pressure dependence of $a$ and $R$ parameters for K$_2$NaScF$_6$:Cr$^{3+}$ are displayed in Fig. 2(a). It should be noted first of all that the calculated values at zero pressure, $a_0$ and $R_0$, compare well with available experimental data. For instance, the obtained $a_0=8.54$ Å figure derived in the present calculations is only 0.8% higher than the experimental one. In the same vein $R_0=1.95$ Å derived for K$_2$NaScF$_6$:Cr$^{3+}$, it is not unreasonable when compared to the $R_0$ values measured for pure compounds containing CrF$_6^{3-}$ units such as K$_2$NaCrF$_6$ ($R_e=1.93$ Å) or Rb$_2$KCrF$_6$ ($R_e=1.94$ Å).

It can be noted in Fig. 2(a) that the relative decrease in $a$
TABLE I. Calculated values of $\beta$ and $n$ exponents for the three elpasolites lattices doped with Cr$^{3+}$. The value of the macroscopic exponent, $m$, is derived through Eq. (4).

<table>
<thead>
<tr>
<th>System</th>
<th>$\beta$</th>
<th>$n$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$NaScF$_6$:Cr$^{3+}$</td>
<td>2.51</td>
<td>4.5</td>
<td>1.80</td>
</tr>
<tr>
<td>Cs$_2$NaYC$_6$:Cr$^{3+}$</td>
<td>2.44</td>
<td>4.5</td>
<td>1.84</td>
</tr>
<tr>
<td>Cs$_2$NaYBr$_6$:Cr$^{3+}$</td>
<td>2.89</td>
<td>4.8</td>
<td>1.66</td>
</tr>
</tbody>
</table>

induced by pressure is clearly higher than that experienced by the Cr$^{3+}$-F$^{-}$ distance. This results confirms, albeit qualitatively, that a change in the lattice parameter due to pressure leads to smaller effects on the hard part of the unit cell. From the calculated $a(P)$ and $R(P)$ curves, the relation between $a$ and $R$ parameters for any value of the pressure is determined. Results are shown in Fig. 2(b) which point out that the relation between $a$ and $R$ is well represented by the law,

$$\frac{R_0}{R} = \left(\frac{a_0}{a}\right)^{1/\beta}.$$  

(3)

The value of the $\beta$ parameter derived from the present calculations for K$_2$NaScF$_6$:Cr$^{3+}$ is found to be equal to 2.5 thus implying that $R$ changes like $V^{1/3.5}$ instead of $V^{1/3}$. In Table I we collected the $\beta$ values calculated for the three elpasolites doped with Cr$^{3+}$, together with the corresponding values of the exponent $n$ reflecting the $R$ dependence of $10Dq$. A behavior quite similar to that displayed in Fig. 2 is encountered looking at the results obtained for Cr$^{3+}$-doped Cs$_2$NaYC$_6$ and Cs$_2$NaYBr$_6$ lattices with values of the exponent $\beta$ close to that found for K$_2$NaScF$_6$:Cr$^{3+}$. It can be noticed that for the three systems, the calculated figures for the exponent $n$ are around 5. A similar conclusion was reached in the work by Brik and Ogasawara.

According to the present analysis, Eqs. (1)–(3) and the $\beta$ values collected in Table I, there is a relation between the macroscopic exponent, $m$, and the microscopic exponent, $n$, given by

$$n = m\beta.$$  

(4)

This simple relation and the $\beta$ and $n$ values of Table I indicate that in the case of Cr$^{3+}$-doped elpasolites lattices, the experimental dependence of $10Dq$ on the sample volume [given by Eq. (1)] should involve a macroscopic exponent, $m$, in the region 1.65–1.85 which is thus much smaller than the microscopic one.

The present study on elpasolites doped with Cr$^{3+}$ thus sheds light on the origin of the anomalous $m=2.3$ value obtained from the experimen tal dependence of $10Dq$ on pressure for LiCaAlF$_6$:Cr$^{3+}$. As the microscopic exponent, $n$ is essentially characteristic of the complex, then using the value $n=4.5$ derived for the CrF$_{6}^{3-}$ unit (Table I) and Eq. (4) we get $\beta=2.0$ for LiCaAlF$_6$:Cr$^{3+}$, a value which is slightly smaller than $\beta=2.5$ calculated for K$_2$NaScF$_6$:Cr$^{3+}$. This result is certainly not unreasonable if one takes into account that the cations involved in the soft part of an elpasolite lattice are all monovalent while in the case of LiCaAlF$_6$ one of such cations is divalent.

The present study thus stresses that the knowledge of the actual value of the $\beta$ parameter from ab initio calculations can be of great help for properly interpreting the experimental pressure dependence of optical, EPR, and Raman spectra of transition-metal impurities in insulating lattices. This knowledge is especially important when the complex formed by the impurity resides in the less compressible part of the unit cell such as it happens for Cr$^{3+}$ impurities in elpasolite or LiCaAlF$_6$ lattices. In fact, taking as a guide the case of the microscopic exponent, $n$, a precise determination of its value by means of extended x-ray absorption fine structure (EXAFS) spectroscopy would require extremely accurate measurements of the changes in $R$ induced by an applied pressure. Bearing in mind that for K$_2$NaScF$_6$:Cr$^{3+}$ a pressure of 5 GPa induces a reduction in $R$ of only 2 pm [Fig. 2(a)] and that the current uncertainties on $R$ values derived through EXAFS technique are at least of 1 pm, a direct measurement of the microscopic exponent seems a rather difficult task to be accomplished. Probably due to this reason no direct measurements of the $R$ dependence on pressure have been reported for LiCaAlF$_6$:Cr$^{3+}$.

Although experimental results for Al$_2$O$_3$:M$^{3+}$ ($M=\text{Cr, Ti, V, and Ni}$) indicate that the $\beta$ exponent is close to one this situation is likely to be no longer true when the $M^{3+}$ impurity replaces a host cation, $Hq^{+}$, with smaller nominal charge ($q<c$). In fact, in cases such as NaCl:Rh$^{2+}$ or K$_2$MgF$_4$:Cr$^{3+}$, the RhCl$_6^{4-}$ and CrF$_6^{3-}$ complexes formed with remote charge compensation are to a good extent elastically decoupled from the rest of the lattice. Thus, for this kind of systems $\beta$ values clearly higher than the unity are also expected.

Before ending this analysis, it should be noted here that the metal-ligand distance of the CrF$_{6}^{3-}$ unit can also be modified by changing the chemical pressure exerted by the lattice on the complex, for example, by changing a host lattice such as K$_2$NaScF$_6$ ($a=8.47$ Å) by another isomorphous one such as K$_2$NaAlF$_6$ ($a=8.09$ Å). The measured increase in the $10Dq$ parameter of the CrF$_{6}^{3-}$ unit on passing from K$_2$NaScF$_6$:Cr$^{3+}$ (10Dq=1.97 eV) to K$_2$NaAlF$_6$:Cr$^{3+}$ (10Dq=2.01 eV) is however only of 0.04 eV. By contrast, a reduction in the lattice parameter of K$_2$NaScF$_6$, $\Delta a = -0.38$ Å, by a hydrostatic pressure would lead, according to Eq. (1) and the calculated $m=1.80$ value, to an increase in $10Dq$ equal to 0.17 eV which is much higher than that found by changing the chemical pressure on the CrF$_{6}^{3-}$ complex. This conclusion is thus in line with previous findings on transition metal impurities in insulating lattices showing that variations in local vibrational frequencies induced by a hydrostatic pressure can be quite different from those produced by changing the host lattice.

Further research on the present issues is now underway.

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