Pressure-induced changes in Cr$^{3+}$-doped elpasolites and LiCaAlF$_6$: Interpretation of macroscopic data

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In the research of pressure effects on Cr$^{3+}$-doped insulating lattices, it is crucial to understand the dependence of the $10Dq$ parameter on the sample volume, $V$. This problem is explored in the present work through $ab$ initio calculations on Cr$^{3+}$-doped K$_2$NaScF$_6$, Cs$_2$NaYCl$_6$, and Cs$_2$NaYBr$_6$ elpasolite lattices as a function of pressure in the 0–5 GPa range. From the calculated values of the lattice parameter and the Cr$^{3+}$-$X^-$ ($X$=F, Cl, and Br) distance, $R$, it is found that $R$ varies with the cell volume, $v_c$, as $v_c^{1/10}$ where $\beta$ lies around 2.6. These results allow one to understand quantitatively the $10Dq$ dependence on $V$ for LiCaAlF$_6$:Cr$^{3+}$ where the measured exponent $m=2.3$ is seemingly anomalous when compared to the values found for ruby ($m=4.5$) or NiO ($m=5$).

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 obtaining $m=4.5$. Values of the exponent $m$ around 5 have also been measured for Al$_2$O$_3$ doped with trivalent cations $^{23}$ such as Ti$^{3+}$, V$^{3+}$, or Ni$^{3+}$.  

From a microscopic standpoint when an impurity, $M^{n+}$, enters an insulating lattice its valence electrons are usually $confined$ in the $MX_N^{N-n}$ complex formed with the $N$ nearest $X^-$ anions.$^{24}$ Along this line, it should be noticed that according to Kohn, the localization of electrons is the fingerprint of every insulating material.$^{25,26}$ Bearing in mind these considerations, it turns out that $10Dq$ for an octahedral $MX_6^{6-n}$ complex macroscopically depends on the $M-X$ distance, $R$. The law describing the $R$ dependence of $10Dq$ derived from theoretical calculations is found to be$^{24-28}$

$$\frac{10Dq}{10Dq_0} = \left(\frac{V_0}{V}\right)^{m/3}. \tag{1}$$

where the $n$ exponent is usually found to lie in the 4–6 region.$^{24}$ The microscopic origin of this strong dependence of $10Dq$ on $R$ has been previously discussed$^{24,29}$ The link between Eqs. (1) and (2) is easily made for NiO or MnO$^{76}$ compounds exhibiting a NaCl crystal structure. Indeed in this simple, lattice structure the cell volume, $v_c$, and thus the sample volume, $V$, are necessarily proportional to $R^3$ thus implying $m=n$.  

However, recent measurements carried out on LiCaAlF$_6$:Cr$^{3+}$ reveal$^{70}$ 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$^{84}$

$$\frac{10Dq}{10Dq_0} = \left(\frac{R_0}{R}\right)^n, \tag{2}$$

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parameter.
TABLE I. Calculated values of $\beta$ and $n$ exponents for the three elpasolite 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>
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</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{NaScF}_6$:Cr$^{3+}$</td>
<td>2.51</td>
<td>4.5</td>
<td>1.80</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{NaYCl}_6$:Cr$^{3+}$</td>
<td>2.44</td>
<td>4.5</td>
<td>1.84</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{NaYBr}_6$:Cr$^{3+}$</td>
<td>2.89</td>
<td>4.8</td>
<td>1.66</td>
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</table>

It can be noted in Fig. 2(a) that the relative decrease in $\alpha$ induced by pressure is clearly higher than that experienced by the Cr$^{3+}$–$F^-$ distance. This result 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,

$$R_0 \frac{1}{R} = \left( \frac{a_0}{a} \right)^{1/\beta}.$$  \hspace{1cm} (3)

The value of the $\beta$ parameter derived from the present calculations for $\text{K}_2\text{NaGaF}_6$:Cr$^{3+}$ was found to be equal to 2.5 thus implying that $R$ changes like $V^{1/2.5}$ instead of $V^{1/2}$. In Table I are 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 10$Dq$. A behavior quite similar to that displayed in Fig. 2 is encountered looking at the results obtained for Cr$^{3+}$-doped $\text{Cs}_2\text{NaYCl}_6$ and $\text{Cs}_2\text{NaYBr}_6$ lattices with values of the exponent $\beta$ close to that for $\text{K}_2\text{NaScF}_6$: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.28

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

$$n = m \beta.$$  \hspace{1cm} (4)

This simple relation and the $\beta$ and $n$ values of Table I indicate that in the case of Cr$^{3+}$-doped elpasolite 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 experimental dependence of $10Dq$ on pressure for $\text{LiCaAlF}_6$:Cr$^{3+}$. As the microscopic exponent, $n$, is essentially characteristic of the complex, then using the value $n=4.5$ derived for the Cr$^{3+}$ unit (Table I) and Eq. (4) we get $\beta=2.0$ for $\text{LiCaAlF}_6$:Cr$^{3+}$, a value which is slightly smaller than $\beta=2.5$ calculated for $\text{K}_2\text{NaScF}_6$: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 $\text{LiCaAlF}_6$ 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 $\text{LiCaAlF}_6$ 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 $\text{K}_2\text{NaScF}_6$: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 $\text{LiCaAlF}_6$:Cr$^{3+}$.

Although experimental results for Al$_2$O$_3$:M$^{3+}$ ($M=$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, $HF^-$, with smaller nominal charge ($\approx c$). In fact, in cases such as NaCl:Rh$^{2+}$ or K$_3$MgF$_4$:Cr$^{3+}$, the RhCl$_{6}^{3-}$ 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 Cr$^{3+}$ unit on passing from $\text{K}_2\text{NaAlF}_6$ to $\text{K}_2\text{NaScF}_6$ ($\Delta a=0.04$ Å) changes by changing the chemical pressure exerted by the lattice on the complex, for example, by changing a host lattice such as $\text{K}_2\text{NaScF}_6$ ($\Delta a=8.47$ Å) by another isomorphous one such as $\text{K}_2\text{NaAlF}_6$ ($\Delta a=8.09$ Å). The measured increase in the $10Dq$ parameter of the Cr$^{3+}$ unit on passing from $\text{K}_2\text{NaScF}_6$:Cr$^{3+}$ ($10Dq=1.97$ eV) to $\text{K}_2\text{NaAlF}_6$:Cr$^{3+}$ ($10Dq=2.01$ eV) is however only of 0.04 eV. By contrast, a reduction in the lattice parameter of $\text{K}_2\text{NaScF}_6$, $\Delta a=0.38$ 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 Cr$^{3+}$ 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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