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_2NaScF_6, Cs_2NaYCl_6, and Cs_2NaYBr_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 $v_c^{(1/3\beta)}$ where β lies around 2.6. These results allow one to understand quantitatively the $10Dq$ dependence on $V^{-m/3}$ 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 ($m=5$).

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During the last decades, the interest in obtaining new tunable solid-state lasers and photoluminiscent materials has greatly promoted the study of optical properties of insulating materials doped with Cr^{3+} ions.[1–3] In this domain of research, particular attention has been paid to the changes in optical properties induced by an applied pressure.[4] Indeed pressure modifies the energy of electronic transitions related to a transition-metal complex, a property widely used for measuring the actual value of pressure in diamond-anvil cells using the Cr^{3+} emission.[5,6] Moreover, in the case of halide host lattices doped with Cr^{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.[7–10]

Among the host lattices used for incorporating Cr^{3+} impurities, a great deal of work has been carried out on those involving a trivalent cation[10–19] such as Al_2O_3, K_2NaScF_6, K_2NaYCl_6, or $LiCaAlF_6$. Indeed in these cases, the Cr^{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 $KMF_3:Cr^{3+}$ or $K_2MF_4:Cr^{3+}$ (M=Mg and Zn) where different centers are simultaneously observed.[8,9,20]

When a hydrostatic pressure, P, is applied on a halide lattice doped with Cr^{3+} it is crucial to look into the variations induced on the cubic-field splitting parameter, $10Dq$. Indeed this parameter alone governs the position of the first spin allowed transition $^4A_2 \rightarrow {}^4T_2$ in octahedral symmetry, and, in particular, its separation with respect to the sharp $^4A_2 \rightarrow {}^2E$ transition as the later is much less sensitive to an applied pressure.[5,6,11] Experimental results obtained on pure insulator materials such as[21,22] NiO or MnO under pressure reveal that $10Dq$ is related to the macroscopic sample volume, V, through the law,

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

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[11] obtaining $m=4.5$. Values of the exponent m around 5 have also been measured for Al_2O_3 doped with trivalent cations[23] such as Ti^{3+}, V^{3+}, or Ni^{3+}.

From a microscopic standpoint when an impurity, M^{c+}, enters an insulating lattice its valence electrons are usually *confined* in the $MX_N^{c\text{-}Na}$ complex formed with the N nearest X^{a-} 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^{c-6a} complex microscopically 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]

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

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 previously been discussed.[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_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[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

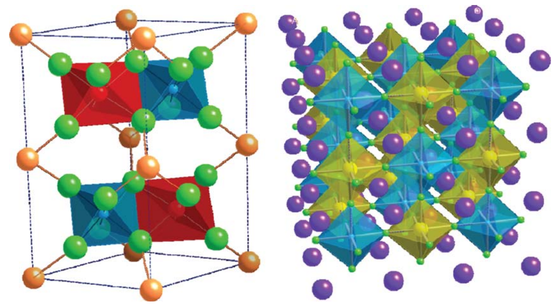

FIG. 1. (Color online) Left: unit cell of the $LiCaAlF_6$ structure, colquiriite-type with trigonal space group $P31c$, showing AlF_6 (blue) and LiF_6 (red) slightly distorted octahedra. Right: cubic elpasolite K_2NaScF_6 structure, with space group $Fm3m$, showing ScF_6 (blue) and NaF_6 (yellow) perfect octahedra. The ratio between the Sc^{3+}-F^- distance and the lattice parameter, a, defines the u parameter.

for $Al_2O_3:M^{3+}$ (M=Cr, Ti, V, and Ni), NiO, or MnO under hydrostatic pressures.[11,21–23] Nevertheless, considering the crystal structure[30] 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, v_c, no longer holds. In fact, in the colquiriite-type $LiCaAlF_6$ structure the CrF_6^{3-} complex (formed under $Al^{3+}\rightarrow Cr^{3+}$ substitution) is embedded in a *softer* region involving monovalent and divalent cations. A similar situation holds for cubic elpasolite lattices such as K_2NaScF_6 (Fig. 1) doped with Cr^{3+} where in the region outside the CrF_6^{3-} complex there are only monovalent cations. Owing to this fact if the lattice parameter, a, of cubic elpasolite host lattices such as K_2NaScF_6, Cs_2NaYCl_6, or Cs_2NaYBr_6 is 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 $10Dq$ 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_2NaScF_6, Cs_2NaYCl_6, or Cs_2NaYBr_6 are cubic,[15] we have first looked into the pressure dependence of both the lattice parameter, a, and the Cr^{3+}-ligand distance, R, for this simpler type of lattice. In order to properly achieve this goal, we report here the calculated pressure dependence of a and R quantities for Cr^{3+}-doped K_2NaScF_6, Cs_2NaYBr_6, and Cs_2NaYCl_6 lattices involving different halide anions. Data corresponding to the first two systems have been calculated for the present work while results for $Cs_2NaYCl_6:Cr^{3+}$ have been derived from the analysis of data conveyed in a previous study.[31]

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.[31] Periodic calculations have been performed by means of plane-wave calculations using pseudopotentials under the framework of the density-functional theory. The Perdew-Burke-Ernzehoff exchange-correlation functional[32] was employed in combination with the Fritz-Haber institute library's pseudopotentials,[33] a $2\times2\times2$ reciprocal-space sampling mesh and a plane-wave kinetic energy cutoff of 40 hartree. The ABINIT code[34] 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 u parameter, characteristic of the elpasolite structure [Fig. 1(b)], have been derived. In a second step, the geometry of $CrX_6M_8Na_6^{11+}$ (X=F, Cl, Br, and I; M=Cs and K) clusters has been optimized to obtain the local geometry around the Cr^{3+} impurity in the three K_2NaScF_6, Cs_2NaYCl_6, and Cs_2NaYBr_6 cubic elpasolites. In this case, the calculations were performed using the Becke-Perdew exchange-correlation functional[35,36] and high-quality basis sets of triple-ζ plus polarization type formed of localized Slater-type functions as implemented in the 2008 and 2009 version of the ADF code.[37] Additional data on the method of calculation can be found in Ref. 31.

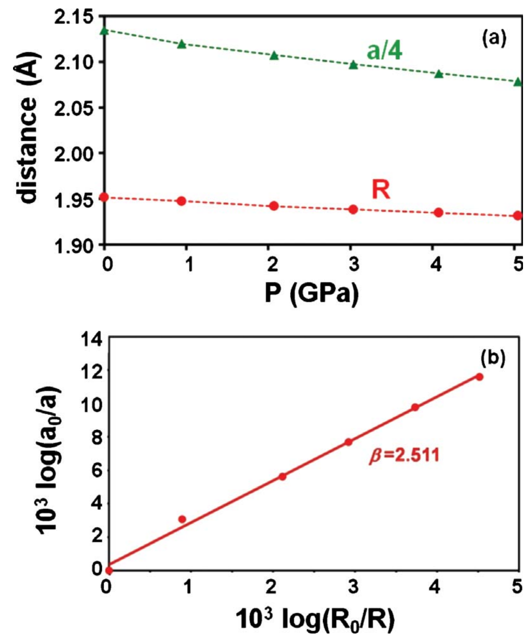

FIG. 2. (Color online) (a) Variation in the lattice parameter, a, and metal-ligand distance, R, in Cr^{3+}-doped K_2NaScF_6 upon applied pressure. (b) Relative variation in the lattice constant with respect to the metal-ligand distance in $K_2NaScF_6:Cr^{3+}$.

Obtained results on the pressure dependence of a and R parameters for $K_2NaScF_6:Cr^{3+}$ 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.[15] 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 $K_2NaScF_6:Cr^{3+}$, it is not unreasonable when compared to the R_0 values measured for pure compounds[38] containing CrF_6^{3-} units such as K_2NaCrF_6 (R_e=1.93 Å) or Rb_2KCrF_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 β and n exponents for the three elpasolite lattices doped with Cr^{3+}. The value of the macroscopic exponent, m, is derived through Eq. (4).

System	β	n	m
$K_2NaScF_6:Cr^{3+}$	2.51	4.5	1.80
$Cs_2NaYCl_6:Cr^{3+}$	2.44	4.5	1.84
$Cs_2NaYBr_6:Cr^{3+}$	2.89	4.8	1.66

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,

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

The value of the β parameter derived from the present calculations for $K_2NaGaF_6:Cr^{3+}$ is found to be equal to 2.5 thus implying that R changes like $V^{1/7.5}$ instead of $V^{1/3}$. In Table I are collected the β 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_2NaYCl_6 and Cs_2NaYBr_6 lattices with values of the exponent β close to that found for $K_2NaScF_6:Cr^{3+}$. 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 β values collected in Table I, there is a relation between the macroscopic exponent, m, and the microscopic exponent, n, given by

$$n = m\beta. \tag{4}$$

This simple relation and the β 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[10] from the experimental 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 $K_2NaScF_6:Cr^{3+}$. 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 β 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 $K_2NaScF_6:Cr^{3+}$ 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,[39] 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[10] for $LiCaAlF_6:Cr^{3+}$.

Although experimental results for $Al_2O_3:M^{3+}$ (M=Cr, Ti, V, and Ni) indicate that the β exponent is close to one this situation is likely to be no longer true[24] when the M^{c+} impurity replaces a host cation, H^{q+}, with smaller nominal charge ($q<c$). In fact, in cases such as $NaCl:Rh^{2+}$ or $K_2MgF_4:Cr^{3+}$, the $RhCl_6^{4-}$ and CrF_6^{3-} complexes formed with remote charge compensation are to a good extent elastically decoupled[40,41] from the rest of the lattice. Thus, for this kind of systems β 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_2NaScF_6 (a=8.47 Å) by another isomorphous one such as K_2NaAlF_6 (a=8.09 Å). The measured increase[19] in the $10Dq$ parameter of the CrF_6^{3-} unit on passing from $K_2NaScF_6:Cr^{3+}$ ($10Dq$=1.97 eV) to $K_2NaAlF_6:Cr^{3+}$ ($10Dq$=2.01 eV) is however only of 0.04 eV. By contrast, a reduction in the lattice parameter of K_2NaScF_6, Δa=−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.[42,43]

Further research on the present issues is now underway.

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