

# Lattice distortions around a $\text{Tl}^+$ impurity in $\text{NaI:Tl}^+$ and $\text{CsI:Tl}^+$ scintillators. An *ab initio* study involving large active clusters.

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*Ab initio* Perturbed Ion cluster-in-the-lattice calculations of the impurity centers  $\text{NaI:Tl}^+$  and  $\text{CsI:Tl}^+$  are presented. We study several active clusters of increasing complexity and show that the lattice relaxation around the  $\text{Tl}^+$  impurity implies the concerted movement of several shells of neighbors. The results also reveal the importance of considering a set of ions that can respond to the geometrical displacements of the inner shells by adapting selfconsistently their wave functions. Comparison with other calculations involving comparatively small active clusters serves to assert the significance of our conclusions. Contact with experiment is made by calculating absorption energies. These are in excellent agreement with the experimental data for the most realistic active clusters considered.

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## I. INTRODUCTION

The interest in luminescent materials has increased in recent years because of their numerous technological applications.<sup>1</sup> Most of these materials involve the doping of a pure ionic crystal, that is substitution of some of the ions by other ions with specific absorption-emission characteristics ( $\text{Tl}^+$ ,  $\text{Ce}^{3+}$ , etc). The presence of impurity ions in ionic crystals induces geometrical distortions in the host lattice. Those distortions are an important ingredient in the scintillation process and thus it is important to establish a reliable description of them.

A convenient way to calculate the lattice distortions is to model the doped crystal by a finite cluster centered on the impurity and embedded in a field representing the rest of the host lattice. This cluster approach has been used to study the geometrical and optical properties of doped crystals.<sup>2–25</sup> The cluster (active space) can be studied by using standard quantum-mechanical methods. The rest of the crystal (environment) can be described in several ways. In the simplest and most frequently used approach, the environment is simulated by placing point charges on the lattice sites, but this procedure has to be improved in order to obtain a realistic description of the lattice distortions around the impurity.<sup>5–8,11,14,17,20,22,23</sup> Model potentials have been developed to represent the effects of the environment on the active cluster, that include attractive and repulsive quantum-mechanical terms aside from the classical Madelung term,<sup>26</sup> but a problem still remains: the large computational cost of conventional molecular orbital (MO) calculations prevents from performing an exhaustive geometrical relaxation of the lattice around the impurity. In the most accurate MO

calculations,<sup>8,20,22,23,25</sup> only the positions of the ions in the first shell around the impurity are allowed to relax. However, geometrical relaxations far beyond the first shell of neighbors can be expected. In fact, recent classical simulations of solids,<sup>27–35</sup> performed employing phenomenological potentials,<sup>36–41</sup> have shown the importance of considering appropriate large-scale lattice relaxations in the study of a variety of intrinsic and extrinsic defects in ionic crystals.

In this contribution we report theoretical calculations of the lattice distortions induced by a  $\text{Tl}^+$  impurity in two well-known ionic scintillators, namely  $\text{NaI:Tl}^+$  and  $\text{CsI:Tl}^+$ . For this purpose we use the *ab initio* Perturbed Ion (PI) model,<sup>42–46</sup> which circumvents the problems mentioned above: (a) The active cluster is embedded in an environment represented by the *ab initio* model potentials of Huzinaga *et al.*<sup>26</sup>; (b) The computational simplicity of the PI model allows for the geometrical relaxation of several coordination shells around the impurity.<sup>11,14</sup>

The remainder of this paper is organized as follows: In Section II we describe the different clusters which have been used in order to assert the influence of the embedding scheme and of the size of the active cluster on the results. In Section III we present and discuss the results of the calculations, and Section IV summarizes the main conclusions.

## II. CALCULATIONAL STRATEGY. DESCRIPTION OF THE DIFFERENT ACTIVE CLUSTERS

The *ab initio* Perturbed Ion model is a particular application of the theory of electronic separability of Huzinaga and coworkers,<sup>47,48</sup> in which the basic building block is reduced to a single ion. The PI model was first developed for perfect crystals.<sup>42</sup> Its application to the study of impurity centers in ionic crystals has been described in refs. 11,14, and we refer to those papers for a full account of the method. In this case, an active cluster containing the impurity is considered, and the Hartree-Fock-Roothaan (HFR) equations<sup>49</sup> of each ion in the active cluster are solved in the field of the other ions. The Fock operator includes, apart from the usual intra-atomic terms, an accurate, quantum-mechanical crystal potential and a lattice projection operator which accounts for the energy contribution due to the overlap between the wave functions of the ions.<sup>50</sup> The atomic-like HFR solutions are used to describe the active cluster ions in an iterative stepwise procedure. Also, as we shall see later in more detail, the positions of some ions in the active cluster are allowed to relax. The wave functions of the lattice ions external to the active cluster are taken from a PI calculation for the perfect crystal and kept fixed during the embedded-cluster calculation. Those wave functions are explicitly considered up to a distance  $d$  from the center of the active cluster such that the quantum contribution from the most distant frozen shell to the effective cluster energy is less than  $10^{-6}$  hartree. In practice, this means 25 shells for NaI:Tl<sup>+</sup> and 21 shells for CsI:Tl<sup>+</sup>. Ions beyond  $d$  contribute to the effective energy of the active cluster just through the long-range Madelung interaction, so they are represented by point charges. At the end of the calculation, the ionic wave functions are selfconsistent within the active cluster and consistent with the frozen description of the rest of the lattice. The intraatomic Coulomb correlation correction, which is neglected at the Hartree-Fock level, is computed by using the Coulomb-Hartree-Fock (CHF) model of Clementi.<sup>51,52</sup> An effective energy can be assigned to each ion that collects all the contributions to the total crystal energy involving that ion.<sup>42</sup>

In this work we have employed several active clusters of increasing complexity and with different embedding schemes. Now we describe each cluster (see fig. 1). First for NaI:Tl<sup>+</sup>, that is, a substitutional Tl<sup>+</sup> impurity in a NaI crystal with the rock-salt structure:

- A) (TlI<sub>6</sub>)<sup>5-</sup>:PC. This active cluster is formed by the impurity cation Tl<sup>+</sup> and its 6 nearest neighbors, whose positions are allowed to relax. The rest of the crystal is simulated by using point charges (PC). Notice that in this case, and also in cluster A\* below, the environment is simplified with respect to the statements at the beginning of this section, in the sense that the “frozen ions” are just point charges.

- B) (TlI<sub>6</sub>)<sup>5-</sup>:NaI. The active cluster is the same as in A, but now the environment is represented by ions whose “frozen” wave functions are obtained from a PI calculation performed for the pure NaI crystal. In the perfect crystal all the cations (or anions) are equivalent, and there is a single nearest-neighbor Na-I distance. These characteristics are lost around the substitutional impurity.
- C) (TlI<sub>14</sub>Na<sub>18</sub>)<sup>5+</sup>:NaI. The active cluster is formed by 33 ions corresponding to the central impurity cation plus four coordination shells. The rest of the crystal is represented by frozen ions with PI wave functions as in B. In the calculations performed on this cluster only the positions of ions in the first shell around Tl<sup>+</sup> are allowed to relax. The other three shells in the cluster provide an interface between the first shell and the frozen environment. The ions in this interface respond to the distortion induced by the impurity by adapting selfconsistently their wave functions to the new potential, but not their positions.
- D) (TlI<sub>92</sub>Na<sub>86</sub>)<sup>5-</sup>:NaI. This is the largest active cluster used for this material. It has 179 ions which correspond to the central Tl<sup>+</sup> cation plus 12 coordination shells. Only the 33 ions of the four inner shells relax their positions; the eight outer shells provide the interface between the inner ones and the environment of frozen PI ions.

Next, for CsI:Tl<sup>+</sup>, that is, a substitutional Tl<sup>+</sup> impurity in a CsI crystal with the CsCl structure, we define four clusters in a similar way:

- A\*) (TlI<sub>8</sub>)<sup>7-</sup>:PC. The active cluster is formed by the impurity plus its eight nearest neighbors, and is embedded in an environment of point charges.
- B\*) (TlI<sub>8</sub>)<sup>7-</sup>:CsI. This cluster is similar to A\*, but the environment is now simulated by frozen ions with wave functions taken from a PI calculation for the pure CsI crystal.
- C\*) (TlI<sub>32</sub>Cs<sub>32</sub>)<sup>+</sup>:CsI. The active cluster has 65 ions and is formed by the impurity plus six coordination shells. Only the positions of the ions in the first shell around Tl<sup>+</sup> are allowed to relax. The environment is the same as in B\*.
- D\*) (TlI<sub>88</sub>Cs<sub>92</sub>)<sup>4+</sup>:CsI. The active cluster has 181 ions: the impurity plus twelve coordination shells. The ions in the six innermost shells can relax their positions, and the environment is as in B\*.

The geometrical relaxations of the shells in the different cluster models described above have been performed by allowing for independent breathing displacements for each shell of ions, and minimizing the total energy with respect to those displacements until the effective cluster

energies are converged up to 1 meV. A downhill simplex algorithm<sup>53</sup> was used. For the ions we have used large STO basis sets: (5s4p) for Na<sup>+</sup>,<sup>54</sup> (11s9p5d) for I<sup>-</sup>,<sup>54</sup> (11s9p5d) for Cs<sup>+</sup>,<sup>55</sup> and (13s9p7d3f) for Tl<sup>+</sup>.<sup>55</sup>

### III. RESULTS AND DISCUSSION

Before presenting the results for the lattice distortions around the Tl<sup>+</sup> impurity we test the consistency of the embedding method for the case of pure (undoped) crystals. For this purpose we compare the results of two sets of calculations for NaI. In the first one we study the clusters labelled A, B, C, D in Section II, with the embedding scheme indicated there for each case, but with a Na<sup>+</sup> cation instead of the Tl<sup>+</sup> impurity. This is, of course, just the case of the pure NaI crystal treated by the embedded cluster method. One can then compare the results with those of a standard PI calculation for the perfect crystal.<sup>42</sup> We can anticipate some differences between the two methods since in the usual PI calculation for a perfect crystal all the cations (or anions) are equivalent, while in the embedded-cluster description of the same system the cation acting as a fictitious impurity and the other cations of the crystal are not described in the same way. This systematic error is, in fact, what we want to remove in the analysis of the distortions around the true, Tl<sup>+</sup>, impurities. If we call  $R_1$  the distance between the Na<sup>+</sup> cation and its first I<sup>-</sup> neighbors, Table I gives  $R_1$  for the four cluster models A, B, C, D, together with the difference  $\Delta R_1 = [R_1(\text{cluster}) - R_1^{PI}(\text{crystal})]$  between the embedded-cluster result and that of the perfect crystal at equilibrium and the relative deviation  $\Delta R_1/R_1^{PI}(\text{crystal})$ . The PI model predicts for the crystal an equilibrium value  $R_1^{PI}(\text{crystal})$  of 3.237 Å, in very good agreement with the experimental value  $R_1^{exp} = 3.240$  Å. The first two cluster schemes, A and B, give large distortions  $\Delta R_1$ . In contrast, a contraction of  $R_1$  smaller than 1 % occurs for cluster models C and D. The conclusions for CsI are similar. A good self-embedding is only achieved for clusters C and D (C\* and D\*). Comparison of B and C shows the importance of a smooth interface between the inner cluster core, where ions are allowed to move, and the frozen environment around the cluster. Comparison of C and D establishes the necessity of allowing for relaxation of the radii of several shells around the impurity. The systematic error that the embedding-cluster scheme makes has to be taken into account in order to interpret properly the distortions induced by the Tl<sup>+</sup> impurity.

Now we present the results for the lattice distortions induced by the Tl<sup>+</sup> impurity in NaI and CsI. In this case we have calculated

$$\Delta R_i = R_i(\text{NaI} : \text{Tl}^+) - R_i(\text{NaI} : \text{Na}^+), \quad (1)$$

where  $R_i$  ( $i=1, 2, 3, \dots$ ) refer to the radii of the first, second, ... shells around the impurity and both calculations

have been performed in the embedded cluster scheme. In this way the systematic errors of the cluster method analyzed in Table I tend to cancel. As before,  $R_1$  is the distance between the central cluster cation, Tl<sup>+</sup> or Na<sup>+</sup>, and the I<sup>-</sup> anions in its first neighbor shell. For the reasons given above we only trust the results from clusters C, D (or C\*, D\*) and the results for  $R_1$  and  $\Delta R_1$  are given in Table II, which also contains results for Tl<sup>+</sup> in CsI. Although we discourage the use of models A and B, just for the purposes of comparison with Berrondo *et al.*<sup>24</sup> we have also calculated  $\Delta R_1$  for NaI:Tl<sup>+</sup> in model A and for CsI:Tl<sup>+</sup> in model A\*. Berrondo used a similar embedded-cluster scheme, although his calculational method was different, based on the linear combination of atomic orbitals (LCAO). Taking as reference the experimental nearest-neighbor Na<sup>+</sup>-I<sup>-</sup> distance in the bulk, Berrondo obtained  $\Delta R_1 = 0.54$  Å, and taking the same reference we obtain  $\Delta R_1 = 0.50$  Å. The good agreement between the two calculations provides a check of our theoretical method. However this large value of  $\Delta R_1$  is partly due to the fact that the calculated  $R_1(\text{NaI:Tl}^+)$  and the reference  $R_1^{exp}(\text{pure crystal})$  are not fully consistent with each other for the reasons discussed above. If we calculate  $R_1(\text{pure NaI})$  also by using model A (with Na<sup>+</sup> instead of Tl<sup>+</sup>), that is, like in eqn. 1, then a corrected “smaller” value  $\Delta R_1 = 0.20$  Å (or 5.6 %) results.

Returning to models C and D we predict, using eq. 1 a lower expansion of  $R_1$ . In fact,  $\Delta R_1$  is equal to 0.039 Å (1.2 % expansion) for model D. However, the distortions are not restricted to the first shell. The second and fourth shells also expand a little, while the third shell suffers a contraction. The expansion of the first and second shells is consistent with the fact that the ionic radius of Tl<sup>+</sup>, equal to 1.40 Å, is larger than the ionic radius of Na<sup>+</sup> (0.95 Å). In summary we find that the structural relaxation around the Tl<sup>+</sup> impurity in NaI is small, although more complicated than usually assumed by previous workers. In fact our calculations suggest that the relaxation could even go beyond the fourth shell.

Let us now turn to CsI:Tl<sup>+</sup>. The calculation with model A\* would give a small expansion  $\Delta R_1$  of the first shell if we take as reference  $R_1^{exp}(\text{pure crystal})$ , and our calculation would then be in agreement with that of Berrondo *et al.*<sup>24</sup> However the ionic radius of Tl<sup>+</sup> is lower than that for Cs<sup>+</sup>, so an expansion of  $R_1$  is not to be expected. By using, instead, eq. 1 we obtained a corrected result  $\Delta R_1 = -0.062$  Å, that is a contraction. Cluster model C\*, in which only the first shell around Tl<sup>+</sup> is allowed to distort, gives a small expansion of  $R_1$  and finally model D\* recovers again the expected contraction. Beyond the first shell,  $\Delta R_i$  oscillates ( $\Delta R_2$  and  $\Delta R_4$  are also negative, while  $\Delta R_3$ ,  $\Delta R_5$  and  $\Delta R_6$  are positive), although the values of  $\Delta R_i$  are very small, in fact smaller than in NaI:Tl<sup>+</sup>.

The conclusion from our calculations is that the distortions around the impurity affect ions in several coordination shells around the impurity, and that consideration of both the atomic and the electronic relaxation of ions

in those shells is required.

For each active cluster we have also calculated the absorption energy corresponding to the intra-atomic transition from the singlet ground state to the triplet excited state of the thallium ion ( $6s^2(^1S) \rightarrow 6s^16p^1(^3P)$ ). Following the Franck-Condon principle, this absorption has to be calculated at the frozen ground state geometrical configuration. Thus, to obtain the energy of the localized excitation, we solve the HFR equations<sup>49</sup> for that geometrical configuration of the active cluster, with the  $Tl^+$  ion in the excited electronic state  $6s^16p^1(^3P)$ , and evaluate the absorption energy as a difference of effective ionic energies:<sup>56</sup>

$$E_{abs} = E_{eff}[Tl^+(^3P)] - E_{eff}[Tl^+(^1S)]. \quad (2)$$

To calculate the contribution of an electronic open shell to the intraatomic energy of a LS electronic configuration, the Hartree-Fock-Roothaan formalism requires the coupling constants of that specific LS term as input. For the description of the open shell ion we have used the coupling constants of the  $^3P$  term as given in ref. 57 and the same basis set as for  $Tl^+(6s^2)$ . The absorption spectra of these doped crystals are more structured (there are several absorption bands); our calculated transitions should be identified with the band A of the absorption spectrum of  $NaI:Tl^+$  (4.25 eV),<sup>58</sup> and with the first absorption band of  $CsI:Tl^+$  (4.27 eV).<sup>59</sup> Both in  $NaI:Tl^+$  and  $CsI:Tl^+$ , the absorption energies we obtain become closer to the experiment as we improve the description of the local geometry around the impurity, as Table II shows. In particular the absorption energies obtained with models D and D\* are remarkably accurate, and this can be ascribed to the accurate representation achieved for the lattice distortion around  $Tl^+$ . Treatment of other absorption bands would require to depart from some of the basic assumptions of the PI model.

#### IV. SUMMARY

We have reported a study of the local lattice distortions induced by a  $Tl^+$  impurity in  $NaI:Tl^+$  and  $CsI:Tl^+$  scintillators. To that end, the *ab initio* Perturbed Ion (PI) model has been used. Large active clusters, embedded in accurate quantum environments representing the rest of the crystal, have been studied. The importance of performing parallel calculations for the pure systems in order to suppress systematic errors from the calculated local distortions has been stressed. The self-embedding performance of the method has been also analyzed with the result that it is necessary to include in the active cluster some shells of ions with frozen positions but able to adapt selfconsistently their wave functions to the displacements of the inner shells. The local distortions obtained extend beyond the first shell of neighbors in  $NaI:Tl^+$ . Thus, the assumptions frequently employed in impurity-cluster calculations, which consider the active space as formed by

the central impurity plus its first shell of neighboring ions only, should be taken with some care. In  $CsI:Tl^+$ , our results indicate that only the first shell suffers an appreciable displacement. Calculated absorption energies are in excellent agreement with the experimental values, and that agreement improves as the description of the cluster becomes more realistic.

Thus, the PI model is able to give a realistic description of the geometrical distortion around a defect in an alkali halide crystal. Of course, the advantages come with some drawbacks: The simplifying assumptions present in the actual version of the PI model make it unsuitable for the study of excited states involving interatomic charge transfer from the impurity. The method also has difficulties for accounting for the crystal-field splitting of open shell excited states. These drawbacks concerning the treatment of excited states should not overlook the essential message of this paper, that is, that the PI method combined with an embedded cluster model allows to obtain accurately the distortion of the lattice around impurity centers in ionic crystals. A combined strategy, namely, PI calculations to obtain the distortions, followed by a MO calculation on the optimized geometry, can be a desirable option in the future.

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## Captions of Tables

**Table I.** Self-embedding test. Values of  $R_1$ , the radius of the first coordination shell around  $\text{Na}^+$  in NaI obtained from embedded-cluster calculations, and their deviations  $\Delta R_1$  from the theoretical value obtained in a PI calculation for the perfect crystal. Relative deviations  $\Delta R_1/R_1^{PI}(\text{crystal})$  are given in brackets. Note the good selfembedding achieved in cluster models C and D.

**Table II.** Distortion induced by a  $\text{Ti}^+$  impurity in NaI and CsI. Distances  $R_i$  ( $i=1, 2, \dots$ ) in Å between the  $\text{Ti}^+$  and its successive coordination shells are given, as well as the differences  $\Delta R_i$  with respect to the values obtained in calculations for the perfect crystal (also with the cluster model) and percent distortions. Last column gives absorption energies (see text) together with percent deviations from the experimental value.

## Captions of Figures

**Figure 1.** The different active clusters studied. Small spheres represent cations and large spheres represent anions. (a)  $(\text{TiI}_6)^{5-}$ ; (b)  $(\text{TiI}_{14}\text{Na}_{18})^{5+}$ ; (c)  $(\text{TiI}_{92}\text{Na}_{86})^{5-}$ ; (d)  $(\text{TiI}_8)^{7-}$ ; (e)  $(\text{TiI}_{32}\text{Cs}_{32})^+$ ; (f)  $(\text{TiI}_{88}\text{Cs}_{92})^{4+}$ . These clusters are embedded in the crystal as indicated in the text.

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NaI:Na <sup>+</sup>	Cluster	R <sub>1</sub> (Å)	ΔR <sub>1</sub> (Å)
	A	3.540	+ 0.303 (+ 9.36 %)
	B	3.159	- 0.078 (- 2.41 %)
	C	3.213	- 0.024 (- 0.74 %)
	D	3.234	- 0.003 (- 0.09 %)

TABLE I.

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NaI:Tl <sup>+</sup>	Cluster	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	ΔR <sub>1</sub>	ΔR <sub>2</sub>	ΔR <sub>3</sub>	ΔR <sub>4</sub>	Abs. (eV)
	A	3.738				+ 0.198 (+5.59 %)				3.91 (-8.00 %)
	C	3.274				+ 0.061 (+1.87 %)				4.19 (-1.41 %)
	D	3.273	4.692	5.510	6.612	+ 0.039 (+1.21 %)	+ 0.075 (+1.62 %)	- 0.054 (-0.97 %)	+ 0.043 (+0.64 %)	4.23 (-0.47 %)
CsI:Tl <sup>+</sup>	Cluster	ΔR <sub>1</sub>	ΔR <sub>2</sub>	ΔR <sub>3</sub>	ΔR <sub>4</sub>	ΔR <sub>5</sub>	ΔR <sub>6</sub>	Abs. (eV)		
	A*	- 0.062 (- 1.62 %)								4.17 (-2.34 %)
	C*	+ 0.013 (+ 0.30 %)								4.21 (-1.40 %)
	D*	- 0.047 (- 1.14 %)	- 0.008 (- 0.15 %)	+ 0.003 (+ 0.06 %)	- 0.016 (- 0.21 %)	+ 0.006 (+ 0.09 %)	+ 0.001 (+ 0.01 %)	4.26 (- 0.23 %)		

TABLE II.













