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ABSTRACT SUBMISSION FORM

Key role of internal electric fields in the properties of ionic materials containing transition-metal complexes

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The properties of insulating materials containing a transition metal cation, M, strongly depend on electrons localized on MX_n complexes formed by M and their first neighbors or ligands, X. Traditionally, these properties have been studied using models that only take into account the isolated complex at the right equilibrium geometry. The main goal of this contribution is to show that a quantitative understanding usually requires to go beyond such models, including the electrostatic potential, $V_R(\mathbf{r})$, produced by the rest of ions of the crystal on the electrons confined in the MX_n complex.

In a first step, we study the microscopic origin of the exotic bright blue colour displayed by the Egyptian Blue pigment ($\text{CaCuSi}_4\text{O}_{10}$) involving square-planar CuO_4^{6-} complexes, the first pigment synthesized by humans, specifically by the Egyptian civilization (~3600 BC) and subsequently used by all Mediterranean cultures. It is stressed that $V_R(\mathbf{r})$ produces a huge red shift of ~1 eV on the highest $d-d$ excitation of CuO_4^{6-} in $\text{CaCuSi}_4\text{O}_{10}$ and the isomorphous Chinese Blue ($\text{BaCuSi}_4\text{O}_{10}$) but not in CaCuO_2 although the $\text{Cu}^{2+}-\text{O}^{2-}$ distance is the same. This extrinsic red-shift due to $V_R(\mathbf{r})$ is shown to be responsible for the blue colour displayed by $\text{CaCuSi}_4\text{O}_{10}$ mainly arising from the presence of SiO_4^{4-} tetrahedra in the compound [1].

In a second step, we show that $V_R(\mathbf{r})$ also plays a key role for understanding the optical properties displayed by impurities with sixfold coordination. So, although the metal-ligand distance, R, is the same for both $\text{BaLiF}_3: \text{M}^{2+}$ and $\text{KMgF}_3: \text{M}^{2+}$ (M = Ni, Mn) and both lattices are cubic 10Dq is ~0.2 eV higher for the former than for the latter, a fact due to the different shape of $V_R(\mathbf{r})$ in the two non-isomorphous host lattices.

Along this line, it is stressed that the different colour displayed by ruby, emerald and alexandrite also reflect the distinct shape of $V_R(\mathbf{r})$ and not differences on the $\text{Cr}^{3+}-\text{O}^{2-}$ distance or covalency [2]. As a salient feature it has been shown that the internal electric field associated with $V_R(\mathbf{r})$ is essentially due only to the first shells of ions surrounding the complex. This internal potential is also behind the distinct optical spectra of C_{4v} and C_{2v} centres involving a close vacancy in $\text{MgO}: \text{Cr}^{3+}$ [3] or the unusual compressed geometry observed in $\text{K}_2\text{ZnF}_4: \text{Cu}^{2+}$ [3].

Finally, the orbital ordering of pure materials with layered structure (such as K_2CuF_4 , La_2CuO_4 , Na_3MnF_6 , CuWO_4 or $\text{Sr}_2\text{La}_2\text{CuTi}_3\text{O}_{12}$) has recently been proved to arise mainly from the internal electric field felt by the transition metal complex [4].

[1] P. García-Fernández et al., *Inorg. Chem.* 54, 192 (2015); [2] J. A. Aramburu et al., *Phys. Rev. B* 85, 245118 (2012); [3] P. García-Fernández et al., *J. Phys. Chem. Lett.* 4, 2385 (2013); [4] P. García-Fernández et al., *J. Phys. Chem. C* 118, 7554 (2014)