

Chemical bonding in high-pressure metal-rich alkali halides

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During the last two decades, it has become possible to investigate materials at very high pressure (hundreds of GigaPascal). This was due to the advent of reliable crystal structure prediction techniques as well as to the improvement of experimental apparatuses. This new possibility has brought to light a completely new realm of chemistry, one in which some textbook concepts need to be abandoned or, at the very least, readapted.

A remarkable example of the unexpected chemical phenomena which occur at high pressure, is the formation of several thermodynamically stable compounds of general formula Na_xCl ($x>1$) [1]. We have carried out a thorough investigation of the electronic structure of these compounds by means of several approaches such as: the Quantum Theory of Atoms In Molecules, the Electron Localization Function, the deformation density and the Density of States analysis. Besides characterizing the chemical bonding of the investigated compounds, our aim is to single out those factors which are mainly responsible for their stability at high pressure. In addition, we carried out crystal structure prediction calculations on metal-rich alkali halides A_3Y ($\text{A}=\text{Li},\text{Na},\text{K}$; $\text{Y}=\text{F},\text{Cl},\text{Br}$) in order to test the predictive ability of the chemical bonding model we derived for Na_xCl compounds. On top of that, the investigation on other alkali halides allowed us to explore if and how their high-pressure behavior is influenced by the identity of cation/anion.

In this contribution we show how the chemical bonding exploration tools mentioned above allowed us to disclose very peculiar chemical features of high-pressure Na_xCl compounds. Examples are the coexistence of metallic and ionic bonds in the same compound and the formation, at very high pressure, of crystal structures where Chlorine atoms form an extended network of bonds through the occupation of their d -orbitals (fig. 1). We will demonstrate how the stability of high-pressure metal-rich alkali halides is mainly determined by two factors: the formation of metallic bonds among alkali atoms and the increase in the number of alkali atoms in the halogen coordination sphere. The external pressure has the effect of changing the energetic balance between these two factors. All the halides of Li and Na follow a common behavior and form similar structures. Potassium, instead, displays a different trend due to the participation of its d -orbitals into chemical bonding. This, for Potassium-containing compounds, becomes an energetically competitive way to obtain the volume reduction which makes them stable at high pressure.

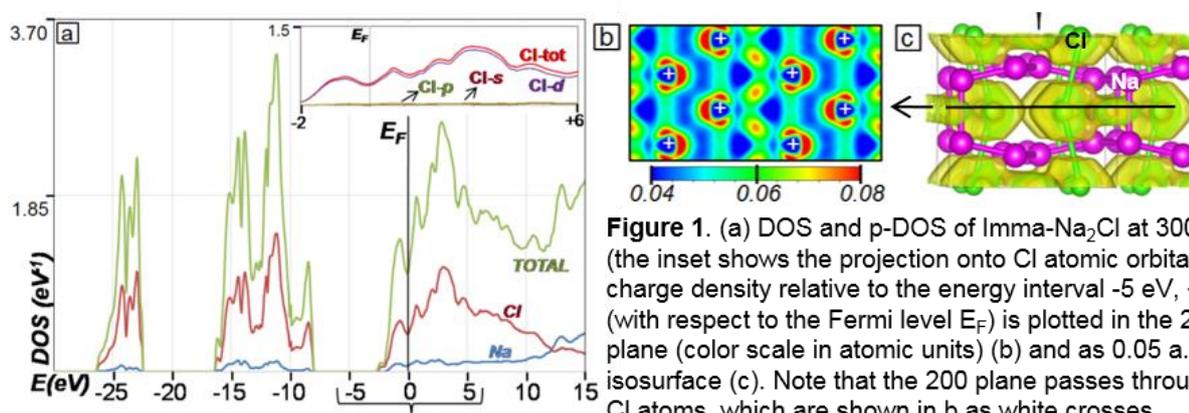


Figure 1. (a) DOS and p-DOS of $\text{Imma-Na}_2\text{Cl}$ at 300 GPa (the inset shows the projection onto Cl atomic orbitals). The charge density relative to the energy interval -5 eV , $+5\text{ eV}$ (with respect to the Fermi level E_F) is plotted in the 200 plane (color scale in atomic units) (b) and as 0.05 a.u. isosurface (c). Note that the 200 plane passes through the Cl atoms, which are shown in b as white crosses.

REFERENCE:

- [1] W. Zhang, A.R. Oganov *et al.* *Science* (2013) 342, 1502-1505