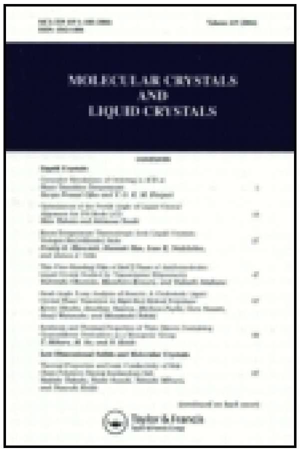

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Importance of Anions in Redox-Type Chimie Douce

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Version of record first published: 04 Oct 2006

To cite this article: Jean Rouxel (1998): The Importance of Anions in Redox-Type Chimie Douce, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 1-4

To link to this article: http://dx.doi.org/10.1080/10587259808045307

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 1–4
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The Importance of Anions in redox-type Chimie Douce

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The interplay between d cationic levels and sp anionic band may result in a partial depopulation of the latter. The holes that are created may associate and lead to anionic catenation with a possible cut-off of the top of the sp band. In any case electrons transferred through an intercalation process will be accepted on levels which are largely anionic in character. Holes at the top of sp bands are at the origin of a nice soft chemistry of the redox type. Their neutralization by electrons allows to stabilize unusual structural types.

Keywords: Intercalation-desintercalation, electronic structures, chalcogenides

When an intercalation reaction takes place a double ion-electron exchange process usually occurs between host and guest species. Cations for example are accepted in empty sites that are present in the structure of a solid compound of a transition element. At the same time this host structure has been reduced by the associated electrons and the d levels of the transition element are usually considered as providing the accepting centers. Three different situations have been described corresponding to three different steps in the delocalization of these electrons (discrete atomic level, "molecular level" of a discrete polyatomic entity, conduction band). This way of thinking is perfectly justified in case of oxides and even sulfides of the elements of the left hand part of the transition periods.

However, when sp "anionic" levels move up (going from oxides to tellurides) and/or d levels drop in energy, anion-cation redox interactions can take place[1].

These interactions largely govern the electronic population in the conducting chains of $NbSe_3$ and, hence, the q vectors associated to the charge density waves instabilities[2]. Their most well known effect is the transition from layered dichalcogenides on the left part of the periodic table to pyrites and marcasites on the right part of it[3]. This transition is in fact the most visible part of a much broader problem which includes evolutions in the layered domain as well as in the pyrite one. The d-sp redox competition results in a partial depopulation of the top of the sp anionic band and a population of the d cationic levels. Holes are created at the top of the sp band. In the pyrite structure they associate under the form of anionic pairs with a cut off of the sp band. One gets a σ_u* band which is empty and will provide the accepting levels when an intercalation process takes place. In any case the depopulation of the top of the sp band which has an important antibonding character results in a shortening of the anion-anion separation. This distance is thus very sensitive to any electronic transfer associated to an intercalation process. On the left part of the periodic table the transferred electrons are accepted by d cationic levels which are above the filled sp band. On the right part of the table they may just refill the top of the sp band. Indeed when holes do not associate at the top of a sp band they allow a nice chemistry of the redox-type. The control of the hole population at the top of the sp band can be well illustrated by copper thiospinels. In $CuCr_2S_4$ there is one hole on the anionic sublattice[4]. In spite of the many sites available one can intercalate only one additional copper. It corresponds to the strict neutralization of the sp band hole by the electron associated to copper (Cu^+). On the other hand one cannot remove copper from $CuCr_2S_4$ to get a layered CrS_2 (of the $CdCl_2$ type). This process would imply an oxidation of chromium (but the corresponding d levels are too deeply engaged in the sp band) or the creation of an other hole at the top of the sp band. Sulfur is probably too electronegative, i.e. the top of the sp band is at a too low energy to stabilize two holes for four sulfides anions. $NaCrS_2$ cannot be deintercalated either. However $NaCrSe_2$ leads to a layered $CrSe_2$[5]. There the holes are stable, the top of the sp band being at a higher energy. Another way to be able to deintercalate is to come back to the left of the periodic table in order to have the d cationic levels moving up. $CuCr_2S_4$ was a mixed valence anionic compound, $CuTi_2S_4$ is a mixed valence cationic compound : $Cu^+Ti^{3+}Ti^{4+}(S^{2-})_4$ instead of $Cu^+(Cr^{3+})_2(S^{2-})_3S^{-\bullet}$. Deintercalation of copper from $CuTi_2S_4$ simply results in the oxidation of Ti^{3+} to Ti^{4+}. The difference in chimie douce between $CuCr_2S_4$ and $NaCrSe_2$ is the position of the top of the sp band. The difference in chimie douce between $CuCr_2S_4$ and $CuTi_2S_4$ is the position of the d levels.

Neutralizing holes at the top of sp band by electrons provided by an electron donor makes it possible to stabilize unusual structural types that would not exist otherwise. This is well illustrated by the $NbGe_xTe_2$[6] and $(LnS)_{1+x}CrS_2$[7] series of phases. The latter can be regarded as infinite two dimensional intercalation compounds with layers of rare earth monochalcogenides separating CrS_2 layers. "Octahedral" chromium disulfide layers similar to those of TiS_2 are stabilized through an electron donation from the LnS sublattice.

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