Jean Rouxel, une mémoire

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Je voudrais remercier mes confrères de l'Institut de Physique et Chimie des Matériaux (maintenant l'Institut Jean Rouxel) pour l'invitation à participer à cette journée d'hommage à Jean Rouxel, parce qu'il n'était pas seulement un homme de science de grande classe, mais aussi, un ami particulier.

Au premier semestre de 1974, je suis resté à l'université de Bordeaux, à l'invitation de Paul Hagenmuller. Au printemps, Paul a arrangé pour moi (et ma famille) une visite au laboratoire de Jean Rouxel. Paul m'a dit : « *Jean Rouxel is a nice man, he will arrange all* ! ». Jean Rouxel a tout arrangé. Cette première visite à Nantes a été agréable et mémorable. Jean était impressionnant : un beau jeune homme, mais avec une rare gravité, et un intérêt fort et vaste pour la chimie. Nous sommes devenu bons amis. (La *figure 1* montre Jean comme je me souviens de lui à cette époque).

Figure 1 - Jean Rouxel (DR).

Jean a fait plusieurs visites à Berkeley où ses conférences ont toujours fait une excellente impression. Nous nous sommes rencontrés à beaucoup de conférences, spécialement aux Gordon Conferences à New Hampshire, États-Unis. A ces conférences, Jean a toujours fait d'importantes contributions.

J'espère que les mots qui suivent, montreront mon admiration pour ses travaux. Maintenant, mesdames et messieurs, je parlerai un peu de l'œuvre de Jean Rouxel, mais pour cela, il est nécessaire pour moi de parler en anglais.

From the beginning of his independent research, Jean Rouxel had a strong well-founded interest in the chalcogenides of the elements. These (chalcogenides) are frequently of low dimensionality with sheet or rod structures. Because of the weak forces that hold the sheets and rods in these structures, it is frequently possible to place other chemical species (usually as ions) between them. As his publications of the late sixties and early seventies show [1-4], Jean and his coworkers were pioneers in this **intercalation chemistry** of chalcogenides which was, early in the 70's, to be driven (by application to electrical-energy storage) into a world-wide interest, with major activities at the Exxon Research and Bell Laboratories in the United States. Indeed, this sudden world-wide interest in the field he had pioneered must have made great difficulties for himself and his coworkers at that time.

The intercalation of species between the rods or sheets (*figure 2*) is often highly reversible, and Jean and his colleagues were soon to exploit this reversibility, by taking species out of layered materials to generate new structural forms. This is a technique known world-wide by the French name « chimie douce », largely because of the pioneering work of Jean and his coworkers. An example is the synthesis [5] by Jean Rouxel and Michel Tournoux of a new form of TiO_2 (which is a metastable material).

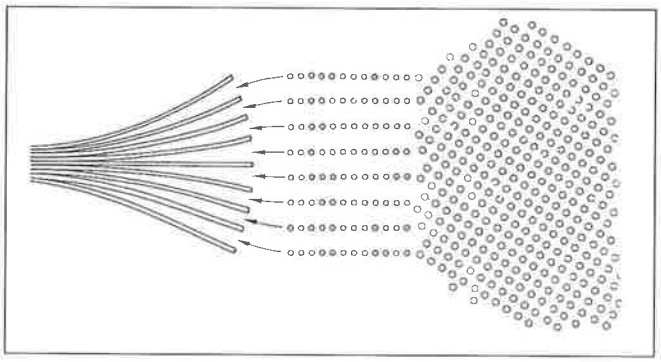

Figure 2 - Chimie d'intercalation : les feuillets de l'édifice lamellaire s'ouvrent pour accueillir diverses espèces ioniques ou moléculaires.

More recently, Jean and his coworkers pioneered chalcogenide MISFIT layer materials [6] where the rigid layer lattice of one chalcogenide is sandwiched between layers of a second material. The repeat unit of one layer is commonly **incommensurate** with the repeat structural unit of the other. The ordering of these chemically and physically different sheets, as Jean was careful to point out, is driven by **electron transfer** from one sheet to its chemically different neighbors (*figure 3*).

Electron transfer from an ion to cation was a theme often emphasized in Jean's writings. He thought deeply and widely on the reasons for the structural changes and the variation in physical properties (*e.g.* electrical conductor or insulator) that went hand in hand with structure and stoichiometry. He was ever asking « *Why is that so* ? » and ever attempting to find more quantitative explanations. We see some of this in what follows under **anion-cation redox competition**. Always, Jean had the underlying fundamental atomic properties of the chalcogen (s and p orbitals) and the metal (d levels) foremost in his mind, when he considered the properties (structural and physical) that a particular chalcogenide adopted (*figure 4*).

We see in *figure 5* a typical piece of Rouxel interpretation. He pointed out that X^{2-} (where X is a chalcogen atom)

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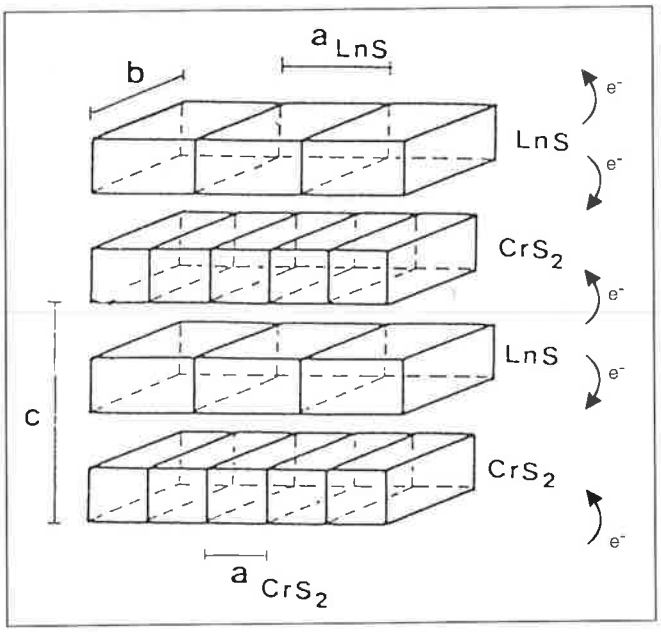

Figure 3 - Misfit compounds : $(LnS)_1 + x(CrS_2)$ misfit compounds show an alternation of LnS slabs (pseudo-NaCl) and CrS_2 ones (TiS_2 type). Incommensurability occurs along a.

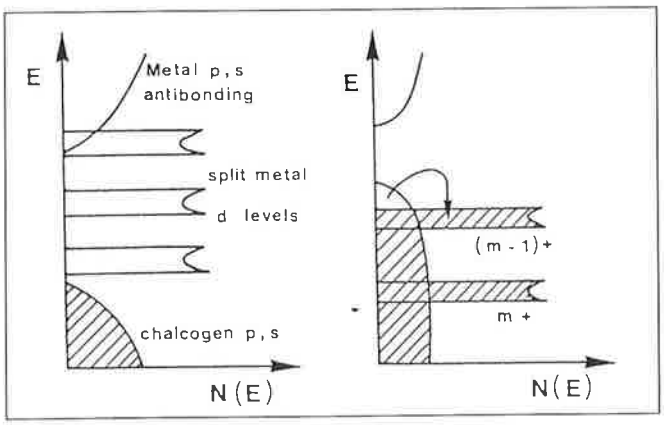

Figure 4 - Anion-cation redox competition and the formation of new compounds in highly covalent systems.

and even X_2^{2-} can provide electrons (*i.e.* each can be oxidized) if the metal orbital-levels are low enough in energy, or the chalcogen (s and p orbital levels) high enough. Because the top of the Te^{2-} sp band lies above the Ti d levels, but not in the case of S^{2-} the d levels are partially filled in $TiTe_2$, but not in TiS_2. This accounts for the metallic behavior of $TiTe_2$ and the semiconducting character of TiS_2. Clearly, very complex behavior can occur (as Jean was careful to point out) when the top of the chalcogen (sp) band and the partially occupied d levels of the metal are degenerate (*figure 4*). This is the situation that occurs in $NbSe_3$ and because this material also has an association with Berkeley through a colleague of mine in the Physics Dept. (Alan Portis) I wanted to say something about it here.

Hair-like crystals of $NbSe_3$ were first made [7] and structurally characterized by Alain Meerschaut and Jean Rouxel in 1974. Quickly, they came into contact with a physics group at Grenoble, that included Pierre Monceau and, together, the Nantes and Grenoble groups made *dc* conductivity and other studies of $NbSe_3$ at low temperature. These

Oxidation of X^{2-} :

$$2\,X^{2-} \rightarrow X_2^{2-} + 2e^-$$

$$X_2^{2-} \rightarrow X_2^- + e^-$$

Impact of the *Electronegativity* of X :

- **as the electronegativity of X *decreases* the anion sp band *increases* in energy**

TiS_2	$TiSe_2$	$TiTe_2$
Semiconductor	Semimetal	Metal

Reduction of M^{X+} :

e.g. in $TiTe_2$ *some* $Ti^{4+} + e^- \rightarrow Ti^{3+}$

- **as M is further to the left in the P. T.,**
- **or in a higher transition series,**
- **the cation levels are increased in energy** *and M^{X+} less easily reduced*

e.g. TiS_2 is $Ti^{4+}(S^{2-})_2$ *but* FeS_2 is $Fe^{2+}(S_2)^{2-}$

$HfTe_2$, *unlike* $TiTe_2$, is *entirely* $M^{4+}(Te^{2-})_2$

Figure 5 - Anion-cation redox competition in chalcogenides X (S, Se.Te).

studies, detailed in the 1975 papers [8, 9], revealed two puzzling low-temperature anomalies in the behavior of $NbSe_3$. Alan Portis takes the story from here. Evidently P. Monceau had taken $NbSe_3$ to Berkeley to look for the microwave Hall effect. Portis was also using microwave loss in single crystals to assess electrical conductivity in an electrodeless way, and this may have been another major reason for the visit of Pierre Monceau, and for his having the $NbSe_3$ with him. A fortuitous mistake (he applied too big an electric field), by Phuang Ong (a graduate student working with Alan Portis) led to the discovery of charge density wave sliding - a novel conductivity.

Ong and Monceau (see the Edward Edelson article [10], the first paragraph of which is excerpted here) were credited with *« the discovery of an entirely new form of electrical conduction in solids... », « whilst studying a new metal that had been synthesized in France the year before »*. Alain Meerchaut and Jean Rouxel were coauthors of the paper announcing this discovery [11]. Indeed, without their synthesis, and the initial collaboration with P. Monceau, this discovery would not have occured. The Ohm's law departures associated with sliding charge density waves below 145 and 59 K have been correlated with the structure. Evidently easy sliding is especially associated with incommensurate charge density waves, such as occur in $NbSe_3$. *Figure 6* shows the structure and the probable association that the different chains of the structural unit have with the charge density waves.

What I have had to say has touched on only a few of the new things that Jean Rouxel did for chemistry. He was a scholar, an innovator, and a persuasive leader in this discipline. His impact, worldwide, will be much missed.

Quand Jean Rouxel est arrivé à la nouvelle université de Nantes, en 1963, il n'y avait rien pour la chimie du solide. Lors de ma deuxième visite, en juin 1990, j'y ai trouvé le nouvel Institut de Physique et Chimie des Matériaux. Je

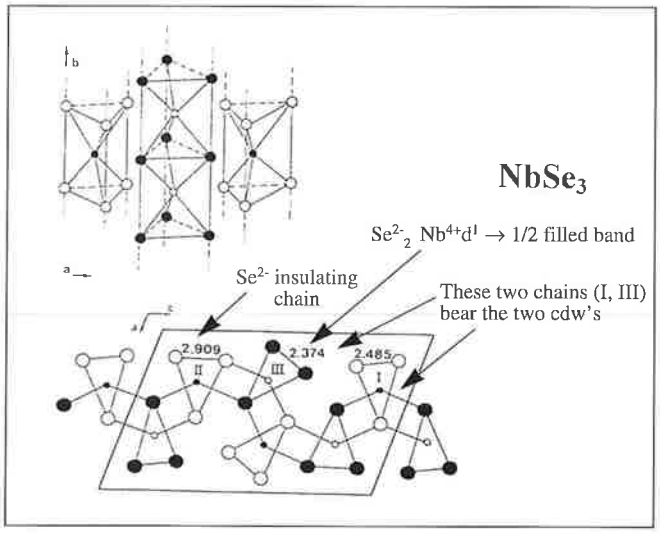

Figure 6 - Anion-cation redox competition. Structure of niobium triselenide : top : adjacent [$NbSe_3$] chains are displaced by b/2 ; bottom : the three types of $NbSe_3$ chains.

crois que cet institut est le propre mémorial de Jean Rouxel. C'est magnifique. C'est un laboratoire de toute première classe mondiale. Mais c'est aussi, parmi les autres, une splendide réalisation de Jean Rouxel.

Références

[1] Danot M., Le Blanc A., Rouxel J., Les composés intercalaires K_xTiS_2, *Bull. Soc. Chim. Fr.*, **1968**, *8*, p. 2670-2675.

[2] Le Blanc A., Danot M., Rouxel J., Sur l'insertion de métaux alcalins, dans la structure CdI_2 du disulfure d'étain, *Bull. Soc. Chim. Fr.*, **1969**, *1*, p. 87-90.

[3] Rouxel J., Danot M., Bichon J., Les composés intercalaires Na_xTiS_2. Étude structurale générale des phases Na_xTiS_2 et K_XTiS_2, *Bull. Soc. Chim. Fr.*, **1971**, *11*, p. 3930-3935.

[4] Bichon J., Danot M., Rouxel J., Systématique structurale pour les séries d'intercalaires M_XTiS_2 (M - Li, Na, K, Rb, Cs), *C.R. Acad. Sc. Paris*, **1973**, *276*, p. 1283-1286.

[5] Rouxel J., Tournoux M., Chimie douce with solid precursors, past and present, *Solid State Ionics*, **1996**, *84*, p. 141-149.

[6] Rouxel J., Meerschaut A., Wiegers G.A., Chalcogenide misfit layer compounds, *J. Alloys and Compounds*, **1995**, *229*, p. 144-157.

[7] Meerschaut A., Rouxel J., Le séléniure $NbSe_3$: obtention et structure, *J. Less-Common Metals*, **1975**, *39*, p. 197-203.

[8] Haen P., Monceau P., Tissier B., Waysands G., Meerschaut A., Molinie P., Rouxel J., *Proceedings of the 14th International Conf. On Low Temp. Physics, Otaniemi, Finland*, summer **1975** (North Holland, Amsterdam, 1975), vol. 5, p. 445.

[9] Haen P., Monceau P., Tissier B., Waysand G., Meerschaut A., Molinie P., Rouxel J., Comparison between electrical conductivity of multilayered $NbSe_2$ and TaS_2 and filamentary compounds $NbSe_3$ and $TaSe_3$, *P.D.L. International Conf. San Juan, Puerto Rico*, Dec. 1-3, **1975**.

[10] Edelson E., Another kind of conductivity, *Mosaic* (N.S.F., États-Unis), **1984**, *15*, p. 26.

[11] Monceau P., Ong N.P., Portis A.M., Meerschaut A., Rouxel J., Electric Field Breakdown of Charge - Density - Wave - Induced Anomalies in $NbSe_3$, *Phys. Rev. Letters*, **1976**, *37*, p. 602-606.