

Jean Rouxel's research between chemistry and physics

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Jean Rouxel was a very personal friend, and therefore I am grateful to be invited to this event in his memory, and to say a few words.

It is great when you mention a scientist's name and everybody is immediately reminded of a landmark that this person has set and, vice versa, you mention the landmark and it is associated with this person right away. When mentioning the name Jean Rouxel the term « chimie douce » comes to mind, and this in a very special sense, as it refers to an important field of research he shaped, but also reflects on him, this very gentle personality. It is with satisfaction to see how in our noisy days this quiet and gentle man came to great honours personally and was able to create an institute which became a world class centre of solid state chemistry.

The work of Jean and his institute which now carries his name is well known and highly respected in Germany. Numerous young chemists from my country were attracted to join the institute as postdocs ; I am happy that my son did so. Quite a number of them went into academia, and in a Europe growing together they will benefit from the open door that this institute offered them. Jean had a love for Germany and took great interest in its historical and present development. And he had a very good knowledge about German chemists and their work. We frequently asked his advice, and his thorough statements were of great help whenever we had to make decisions for universities or the Max-Planck Society.

Jean and I met for the first time 25 years ago. There were many occa-

sions to see each other on conferences and mutual visits. We shared ideas and had fun in learning about new results, however, our real scientific cooperation started late, actually five years ago, when he came to Stuttgart as a Humboldt awardee. We always had a common interest in structure property relations. Without going into any detail, I should like to sketch the columns on which Jean's research into this borderline field between chemistry and physics rested.

In the Hund-Klemm lecture on « Electronic factors for the design of low-dimensional solids » which Jean gave in our institute, he illustrated one very strong column, namely his comprehensive interest in low-dimensional systems [1]. When giving his inaugural lecture in the Collège de France, he used the comparison with a book. The single pages are firmly kept in place, however, their mutual contact is loose, and one can put additional papers between the pages. The more accurate term for putting papers between the pages is intercalation, and just one example [2] out of a large number of publications which deal with the insertion and withdrawal of atoms in low-dimensional structures and the rationales behind may be taken as a representative. Intercalation reactions form the second column. A paper between the pages, if it is too large, will stick out, however, in a crystalline solid a misfit will occur, and the rigid substructures will influence each other. This leads to the third column, that of structural misfit [3].

Last, but not least, another strong column adds to the three others which does not seem to be related to them on first sight, but in fact is intimately related. The individuals in a community have to arrange with each other : as the

substructures have to adjust for a certain mechanical misfit, they also have to seek an electronic balance. The last column to be mentioned is the cationic-anionic redox competition [4].

Let me cast this view into a picture with the different columns I mentioned (figure 1), and in the following exemplify this picture by focussing on one

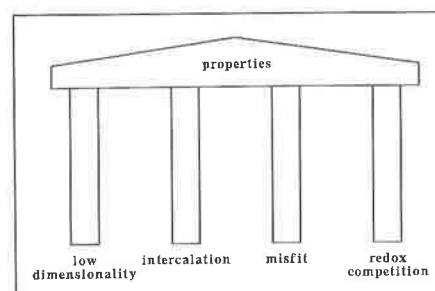


Figure 1.

special property, superconductivity. Before entering this topic, a general remark might be appropriate. Many of us will have made the experience that we think about independent problems and then all the sudden realize that it is one and the same problem. Reading through Jean's publications there are all these logic steps from insight to insight. But there are also starting points which seem to bear no relation, and it is only afterwards that we realize seemingly remote views to coincide. The same is obviously true when one seeks for an understanding of superconductivity. The starting points that I shall illustrate seem to bear no relation whatsoever with the actual phenomenon. The ideas to be briefly outlined are of a very early origin.

The discovery that light comes along in small energy packages, so is of a quantized nature, started quantum theory in 1900. Figure 2 shows Max Planck's famous formula in his own handwriting. In spite of its revolution-

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$$E_0 = \frac{2\kappa_0^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$

Figure 2.

any character which changed science dramatically, the formula is based on classical grounds, for example, on the assumption of an ether. Nearly 25 years later a great Indian physicist, Satyendra Nath Bose, suggested a new approach to derive Planck's formula without those traditional assumptions that Planck had used. Albert Einstein translated the manuscript into German for publication in « *Zeitschrift fuer Physik* » [5], and he got himself heavily involved in the matter. Einstein generalized the theory extending it from radiation to the quantized behaviour of a gas. In his lengthy publications [6] on a quantum theory of monoatomic ideal gases, Einstein claims that an increasing density of the gas leads to the consequence that an increasing number of atoms will enter **one** quantum state, a state without kinetic energy. Normally, a gas loses its volume when it condenses. Here it condenses into a state of zero momentum.

Again, much later, in 1938, Fritz London thought about the consequences of Bose-Einstein condensation [7]. The essence of his treatment was that the condensation leads to a phase change at a critical temperature. If there is a fraction of particles - in a gas or in the electron gas of a metal - which have zero velocity, then in Bose-Einstein statistics the fluidity or conductivity approaches infinity below this critical temperature. In a very careful way, he points out that this could be a possible explanation for superfluidity and superconductivity.

Now a chemist, Richard Andrew Ogg, had **the** idea 8 years later [8]. Photons are spin-free, and they obey Bose-Einstein statistics. How can the conduction electrons in a metal be made spin-free in order to obey the same statistics? They need to form pairs with opposite spins. Ogg claimed to have found superconductivity up to 190 K in quenched metal-ammonia solutions (back in 1946 !). His results, however, could not be reproduced by others and he was much teased for his idea. Sad enough, he found a tragic end by committing suicide.

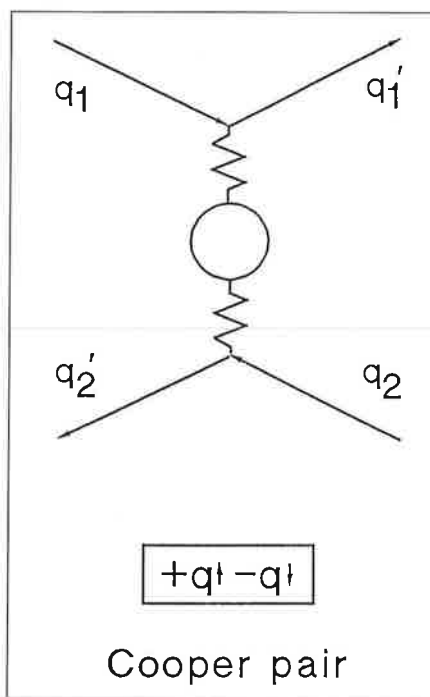


Figure 3.

The paired state was then forgotten and rediscovered 10 years later by Cooper, hence it is now called Cooper pair. An electron represented by its momentum \mathbf{q} is coupled with another one through the lattice of the superconductor (figure 3). In the theory of Bardeen, Cooper and Schrieffer, the interaction occurs via lattice vibrations, phonons [9]. The ground state of superconductivity is characterized by the fact that the momenta \mathbf{q} and $-\mathbf{q}$ cancel. The pair has zero momentum (zero velocity) and the two spins compensate each other. Such pairs, whether preformed or forming upon cooling obey the criteria for Bose-Einstein condensation as worked out in London's paper.

Of course, the physicist's model does not tell anything about the chemical ingredients for a metal to become a superconductor. The logo of an empty sphere (sometimes filled with a plus sign to indicate the positively charged atomic cores) is the only hint to chemistry, hence there is no chemistry in the model. Yet, the formal description of the Cooper pair bears some similarity to the formal description of a chemical bond. When we draw a line between two atoms A and B in a two-centre bond, this represents two electrons with opposite spins and net momentum zero as these electrons are localized in the bond. Is there any connection between superconductivity

and a tendency of conduction electrons for pairwise localization in a bonding, nonbonding or antibonding configuration which results in a pairwise attractive interaction?

Let me illustrate the basic idea [10] which Jean and I shared and frequently discussed, and let me first introduce our model system (figure 4). The structure of $\text{Y}_2\text{Br}_2\text{C}_2$ is closely related to many of Jean's low-dimensional solids. Double layers of rare earth metal atoms offer voids for the accommodation of C_2 units, and these layers are sandwiched by halogen atoms. The characteristic structural element is a slab of atoms stacked upon one another and glued together via van der Waals bonds.

C_2 units in a solid are known to every chemist from calcium carbide, the former main source of acetylene. Indeed, the solid contains a triply bonded C_2^{2-} ion with $d_{\text{C-C}} = 120$ pm. The larger C-C distance in yttrium carbide bromide $d_{\text{C-C}} = 128$ pm comes near to a double bond distance in agreement with a reasonable distribution of electrons between the atoms according to $\text{Y}^{3+}_2\text{Br}_2\text{C}_2^{4-}$, described as in an ethenide. These assignments are easily verified in an extremely simplified view of the chemical bonding of the C_2 units in these solids (figure 5).

When combining two carbon atoms, their s and p orbitals mix to form eight bonding or - marked by an asterisk - antibonding orbitals. In addition to the eight carbon electrons, there are two more in the case of CaC_2 and four more with the layered carbide bromide, leaving three and two antibonding states unoccupied, according to a triple bond and a double bond, respectively. So far, everything looks much the same in both cases. However, there are dramatic differences, and again we get right into the heart of Jean's extended work on cation-anion redox systems.

In the case of CaC_2 the two electrons in the highest occupied orbital stay with the C_2 unit, they are strictly localized and, hence, CaC_2 is a colourless insulator. However, in the case of $\text{Y}_2\text{Br}_2\text{C}_2$ empty d states of the metal lie near to the filled π^* allowing for a backdonation of electrons from the C_2 units to the metal atoms which results in an electronic delocalization, bronze-like colour and metallic behaviour. Mind,

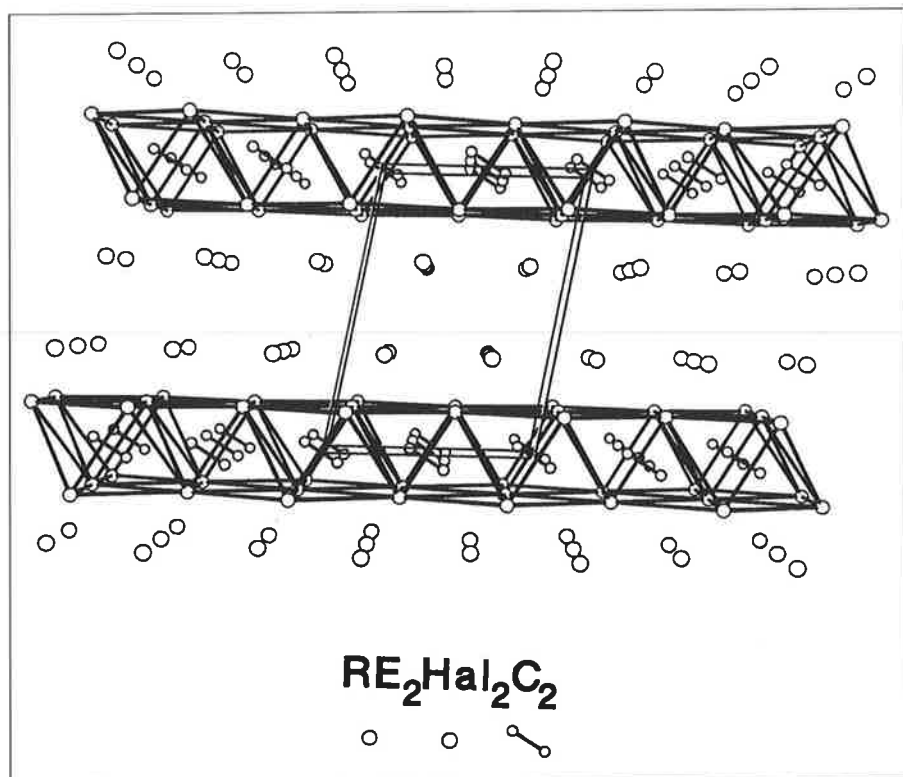


Figure 4.

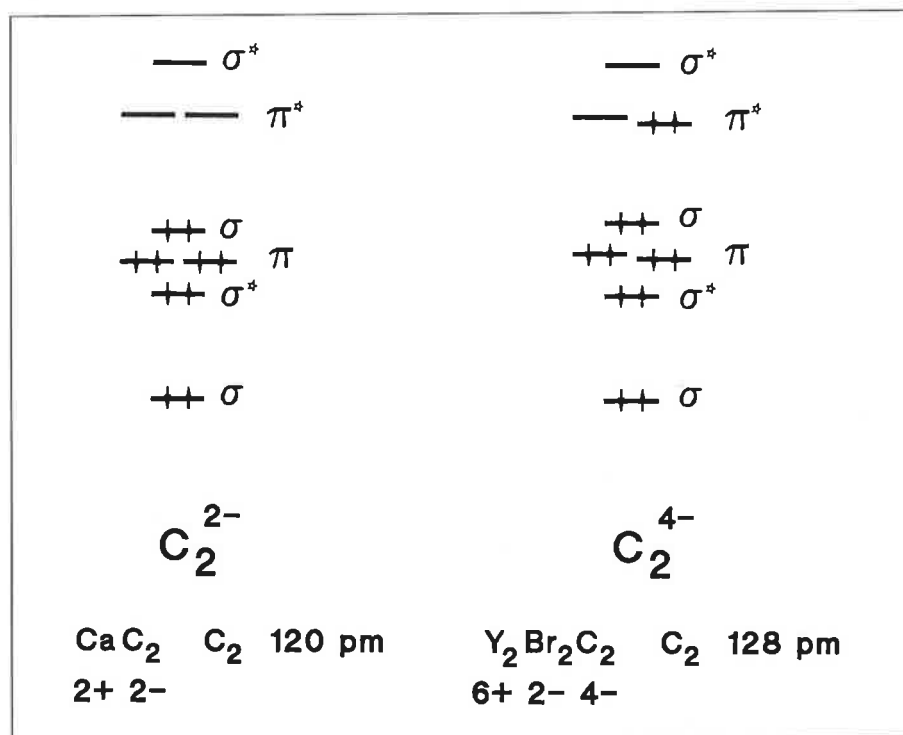


Figure 5.

the compound is a metal by accident, very near to a localized system, and it becomes superconducting at low temperature as indicated by the electrical resistivity and the behaviour in magnetic fields (figure 6).

Using Jean's terminology, let me repeat the argument for the occurrence

of metallic and superconducting properties in this material (figure 7) : the redox competition leads to a charge transfer with electronic delocalization and metallic properties. However, there is the quasi molecular π^* state which attracts conduction electrons pairwise and leads to superconductivity. One

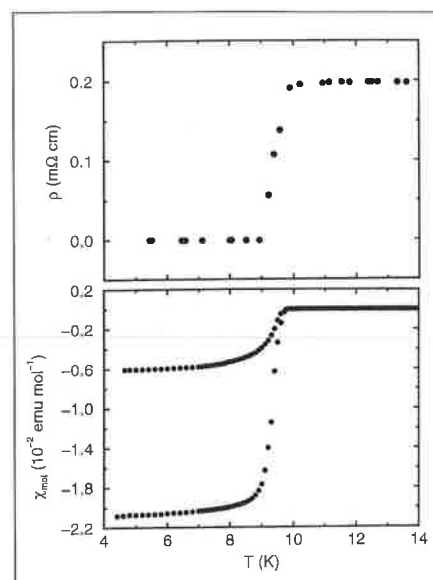


Figure 6.

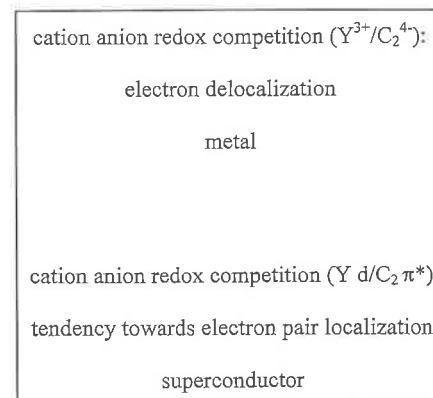


Figure 7.

can address these assumptions via band structure calculations to see whether the normal state offers certain conditions which meet these assumptions and are a preposition to superconductivity (figure 8).

There are conduction electrons in bands of very different character. Steep

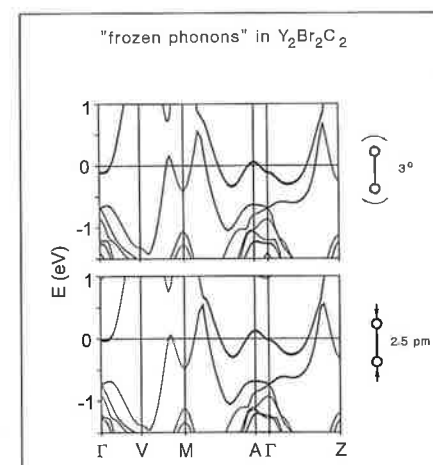


Figure 8.

bands indicate high velocity, flat bands small velocity, approaching zero with a zero slope of the band. The flat band at Fermi energy E_F exhibits considerable π^* character as indicated by the scaled line width. The conduction electrons in this band meet the London criterion by approaching zero velocity. Now we want electron pairs, and it can be seen that small dynamic distortions like changes to the C-C distance or tilting of the C_2 units may provide the spin pairing energy. So, single electron pairs with zero velocity are present which meet the scenario of Bose condensation as worked out by London.

Due to the low-dimensional character of the material, there are a number of experimental possibilities to play with, and many of them closely follow the kind of research which is associated with the name of Jean Rouxel. A straight forward experiment is the replacement of the bromide by smaller chloride or larger iodide ions, thus squeezing or expanding the metal atom cage around the C_2 unit to change the overlap and hence the redox equilibrium. In a general sense this comes near to the idea of structural misfit in its mutual dependence of substructures. Indeed, T_c follows such modification in a smooth way (figure 9). The cation-anion redox system is obviously optimized for superconductivity in a compositional range between the bromide and the iodide.

Of course, the layer-like structure offers yet another possibility. Placing sodium into the van der Waals gap would inject electrons into the layer and thus change the relative position of the π^* state. Intercalation chemistry was Jean's very own field, and we had a good cooperation [11]. It turned out that intercalation works well in this halide system (figure 10). T_c is raised with intercalation of sodium. Obviously, it is beneficial for superconductivity when the depletion of the π^* state through redox competition is compensated towards full occupancy.

Let me come to an end. If the arguments for the origin of superconductivity in these layered systems are general, one expects CaC_2 to become a superconductor when the metal is repla-

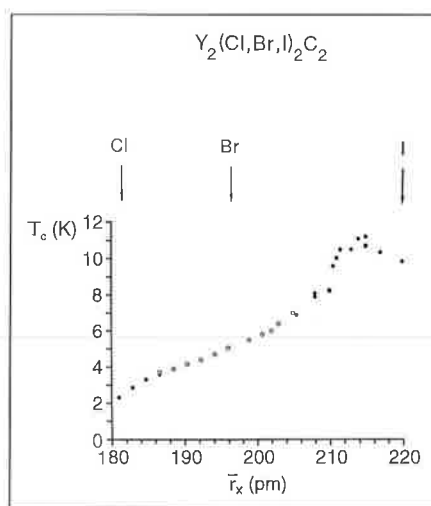


Figure 9.

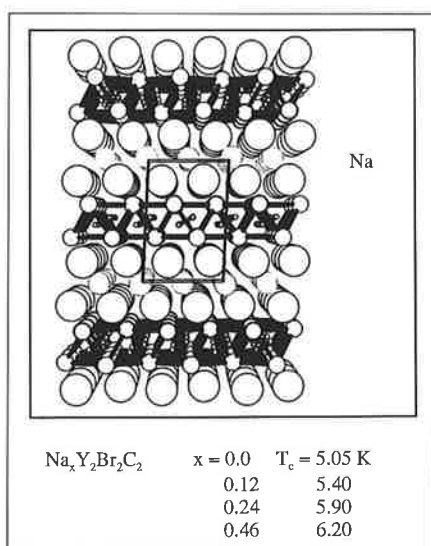


Figure 10.

ced by another one with more valence electrons, because then the electronic level is raised to the π^* orbital. Indeed, it works! YC_2 is a superconductor.

There is a large amount of literature data on superconductivity in rare earth carbides which we can now use to test our idea (figure 11). In order to do so, the general phase compositions taken from literature are rewritten and normalized to C_2 . Then we count, how many electrons are available to be transferred to C_2 . The result is most interesting: superconductivity is restricted to those phases which allow for C_2 units, it starts with the occupation of the π^* level of the C_2 unit and reaches a maximum in T_c again with four electrons per C_2 . To be more precise, slightly more than four electrons seem to be best.

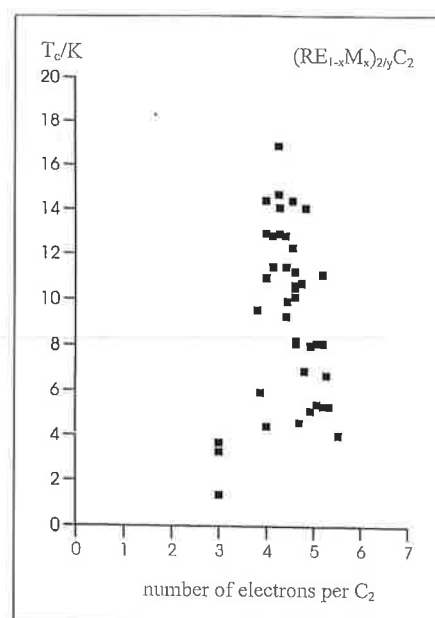


Figure 11.

Hence, in spite of entirely different compositions, structures and dimensionalities of structures, the rare earth carbide halides and the carbides even agree in the detail that the C_2^{-4} ions want to be slightly diving in the sea of conduction electrons in order to pair the electrons most efficiently.

My friendship with Jean Rouxel was long standing. Our scientific cooperation started late. It was terminated through his sudden death. I do hope that there will be ongoing cooperations with my French colleagues and friends in the spirit as it was created by Jean.

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