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What Is the Metallic Bond?

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Solids have for many years been categorized in terms of their bonding type: ionic, covalent, van der Waals, and metallic. Particularly useful in a pedagogic sense have been the diagrams devised[1,2] by van Arkel and Ketelaar (**1**) which effectively place compounds into three out of the four categories. Recently the demonstration[3] that the use of electronegativity scales based on experimental multiplet-averaged ionization energies[4] enables quantitative delineation of the regions of this diagram has focused attention on the meaning of one of these classifications, namely, the "metallic bond". What is its description in terms of the ideas of chemical bonding developed since the presentation of the original ideas behind the van Arkel–Ketelaar scheme? To be added to the data base for discussion are the many metallic materials discovered in the past 40 years. They include the substantial number of molecular metals held together by van der Waals interactions, exemplified most recently by the doped fullerenes, and the metals (and sometimes superconductors) generated by the doping of solids traditionally regarded as "ionic", such as $La_{2-x}Sr_xCuO_4$. This paper places metallic systems firmly in the realm of compounds described by the orbital model, of widespread utility in describing both molecules and solids. We will suggest that that the term "metallic bond" be dropped from chemical use.

There is perhaps no pair of words with such a variety of meanings as exists in chemistry for the term "delocalized" and its antonym "localized", and so one should be careful with their use. Metals are frequently described by delocalized bonding because they are electrical conductors (and thus contain itinerant electrons), and insulators often by localized bonding since they are not. However, one can be much stricter in the choice of language and should be. First, consider the very broad spectrum of systems for which the Mulliken–Hund or molecular orbital picture is appropriate. Within the umbrella of Hückel theory these include both the σ and π manifolds of organic systems, including the "delocalized" picture for the π systems of conjugated polyenes. Also, well-described by such an approach are not only the electronic structure of materials such as diamond and the true Zintl phases[5] but also those of metalloids such as bismuth. Such a picture also leads to identification of the factors behind the interesting observations concerning the change under pressure of the conducting properties of the "typically metallic" group 2 metals such as calcium.[6] The link between the two is well-known.[7] If in a molecule there are a set of N bonding orbitals each occupied by an electron pair, and there are N close contacts in the structure, then frequently a set of N localized two-electron, two-center bonds may be generated by taking linear combinations of the delocalized orbitals. The structure of methane is the quintessential example with its four "bonds" and its filled $a_1 + t_2$ orbital set. If there are insufficient pairs of electrons for such bonds, as in the π manifold of benzene for example, then such a transformation is not possible. In this case the organic chemist draws a circle inside the hexagon to describe this state of affairs. An exactly analogous picture holds for solids. The band structure of diamond may be localized in the same way as for methane by the construction of Wannier functions.[8] Taking linear combinations of the orbitals at the zone center and zone edge of the band structure of a chain silicate leads to construction of a localized picture.[9] However, for the band structure which describes the conduction electrons of molecular metals, such a transformation is not possible and the delocalized picture has to be used.

There are other instances where there is no choice in electronic description. A localized wave function leading to insulating behavior can result from the presence of an on-site Coulomb repulsion larger than the interaction between orbitals on adjacent sites.[10] A simple example is that of a collection of atoms at large internuclear separation. If this is the case, then the localized description is the only one that may be used.

Thus the option of an electronic description in terms of localized orbitals is available only for a subset of Mulliken–Hund systems. The delocalized picture is always appropriate, and recognition of this fact has led in the molecular realm to valuable electronic descriptions of a wide range of compounds, especially organometallic ones in recent years.[11] This leads to one view of the "metallic bond". It simply corresponds to a Mulliken–Hund description but without the option of the construction of localized Wannier functions. Since the construction of such functions requires[8] the presence of a filled band of electrons, in more general language a metal corresponds to the presence of a partially filled energy band. Thus there is no special type of chemical bonding associated with the "metallic" bond, and it is our opinion that the term should be dropped from the literature. But what leads to partially filled bands of this type for some systems and not for others, and why does the van Arkel–Ketelaar scheme work so well?

Partially filled energy bands are in principle subject to Fermi surface instabilities described as charge density wave (CDW) or Peierls distortions which, as the structure changes, open a gap at the Fermi level and may create an insulator or semiconductor.[12] Many CDW instabilities are triggered by lowering of the temperature and occur in a range of systems which cover a wide range of chemical types, metal oxides and sulfides, molecular metals, and the elements themselves. We have described, for example the structures of the group 15 elements in terms of three-dimensional Peierls distortions[13] of the (metallic) simple cubic structure. As a result of the distortion in phosphorus the coordination number is reduced from 6 to 3, the three "sp^3" bonds of the localized model. In this case the distortion may be reversed under pressure. Black phosphorus becomes a metal under pressure.[14] In an exactly analogous way an infinite chain of hydrogen atoms distorts to give a set of dimers in which the atoms are linked to each other by a conventional σ bond.[15] Thus one criterion for the generation of a metal is the presence of a partially filled energy and the impotence of CDW distortions which will open a gap and enable a localized picture to be drawn. Of importance therefore in understanding the origin of the character during horizontal excursions across the van Arkel–Ketelaar

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(1) Ketelaar, J. A. A. *Chemical Constitution; An Introduction to the Theory of The Chemical Bond*, 2nd ed. Elsevier: Amsterdam, 1958.

(2) van Arkel, A. E. *Molecules and Crystals in Inorganic Chemistry*; Interscience: New York, 1956.

(3) Allen, L. C. *J. Am. Chem. Soc.* **1992,** *114,* 1510. Allen, L. C.; Capitani, J. F.; Kolks, G. A.; Sproul, G. D. *J. Mol. Struct.* **1993,** *300,* 647.

(4) Allen, L. C. *J. Am. Chem. Soc.* **1989,** *111,* 9003.

(5) Levin, A. A. *Solid State Quantum Chemistry* McGraw-Hill: New York, 1977.

(6) Brennan, T. L.; Burdett, J. K. *Inorg. Chem.* **1993,** *32,* 750.

(7) Dewar, M. J. S. *Theory of Molecular Orbitals*; McGraw-Hill: New York, 1969.

(8) Haug, A. *Theoretical Solid State Physics*; Pergamon Press: New York, 1972.

(9) Burdett, J. K. In *The Stability of Minerals*; Price, G. D., Ross, N. L., Eds.; Chapman and Hall: New York, 1992.

(10) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Saunders: Orlando, 1976.

(11) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(12) Canadell, E.; Whangbo, M.-H. *Chem. Rev.* **1991,** *91,* 965.

(13) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1983,** *105,* 1079.

(14) Jamieson, J. C. *Science* **1963,** *139,* 1291.

(15) Burdett, J. K. *Prog. Solid State Chem.* **1984,** *15,* 173.

0002-7863/94/1516-8808$04.50/0

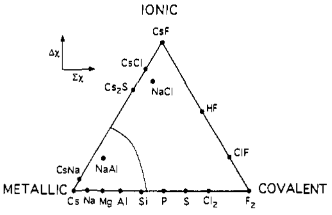

Figure 1.

diagram is an appreciation of how the driving force for such a distortion varies across the periodic table.

In terms of the factors which govern the magnitude of the distortion, it should be recognized that the Fermi surface instability comes via the occupied energy levels which lie at highest energy. Resisting the distortion, driven by these electrons, are the "elastic" forces of the underlying electornic structure and the repulsive part of the potential. Using an interatomic potential of the Lennard-Jones type, $V = -A/r + B/r^n$, the total energy at equilibrium for a one-dimensional chain of atoms with interatomic separation a is $E = -[A/a][1 - (1/n)]$. Alternate compression and expansion of adjacent linkages by $\pm\Delta a$ leads to a new energy, $E = -[A/a][1 - (1/n)] + nA(\Delta a/a)^2$, a function minimized for $\Delta a = 0$. A similar result is found for a system of Hooke's law springs. Keeping the cell "volume" constant during the distortion always favors the symmetrical metallic structure.

This model may also be used to understand why the application of pressure frequently reverses the stability of the parent and Peierls distorted structures. From the simplest discussion of Peierls distortion using Hückel tight-binding theory,[15] the distorted structure is always more stable whatever the pressure. The energy changes just scale with changes in the interatomic hopping intergral, t, or Hückel β. This result remains true even if second-nearest neighbor interactions are included. The difference in repulsive energy between the symmetrical and distorted structures is proportional to $a^{-n}(\Delta a/a)^2$, the repulsion being less fierce for the former. Thus, under conditions where it is the repulsive part of the potential which dominates (as a becomes smaller), the symmetric structure becomes moe stable. Increasing the pressure therefore can lead to a reversal of the Peierls distortion.

In order to quantify the ideas of the previous section we have performed some simple tight-binding band structure calculations of the extended Hückel type. We wish to gain insight into the result of moving from left to right on the diagram in Figure 1, which leads from metals to insulators. Thus elemental lithium has a close-packed structure (a low temperatures and a pseudo-close-packed one (bcc) at higher ones) and is a metal, but elemental fluorine is an insulator and a molecular solid composed of F_2 dimers. The calculations were set up to compute the energy difference between one-dimensional chain of atoms (we included linear, zigzag and spiral chains) and the pseudo-dimer structure where nearest neighbor interatomic separations were alternately decreased and increased by 10%. Also included were distortions of the simple cubic structure which lead to the observed structures of the elements of groups 14 and 15. Although the calculations are crude, they mimic experiment very well. Using standard parameters[16] the energies of distorted and undistorted structures were always close for lithium. For example, the undistorted one-dimensional chain was favored by 0.02 eV/atom over its distorted variant. For fluorine the situation was very different; the analogous distorted structure was favored by 0.82 eV/atom.

There are a number of contributions to this result, and the tight-binding method is an ideal one to sort them out. The increased number of valence electrons on the right-hand side of the table plays a role. In order to see how important this is, calculations were performed on a carbon chain (halfway between Li and F) with a varying electron count. The calculated stabilization of the distorted structure was found to be 0.31 eV for an electron count appropriate for lithium, and by over 10 times this number if the fluorine electron count was used. Thus increasing the number of electrons increases the driving force for the insulating state, via the number of electrons in filled levels which are stabilized during the distortion. Clearly, though, the orbital parameters appropriate to each case are important, too. The part of the electronic picture which is easiest to see is that associated with the off-diagonal matrix elements, H_{ij}. These will determine the energy scale associated with the distortion. Using the Wolfsberg-Helmholz approximation[17] these are written as being directly proportional to the sum of the corresponding diagonal ones. Since the H_{ii} values increase smoothly on moving from left to right across the periodic table, an increase in the magnitude of the distortion energy, and thus the distortion itself, should be expected from this source. This is readily reproduced by calculation. The H_{ii} values used in calculations of this type come from atomic spectral data. It is thus particularly interesting to see that Allen's horizontal index for his modern-day van Arkel–Ketelaar diagram is just the sum of the atomic electronegativies evaluated[4] from the same atomic data. A third consideration is most important for the elements at the left-hand side of the table where, as shown elsewhere,[6] the s, p interorbital interactions are large compared to the s/p separation, and the top of the "s band" for these metals in fact is p–p bonding rather than s–s antibonding. The orbitals themselves are diffuse and interactions with second-nearest neighbors non-negligible. It is a combination of these effects which is behind the results for lithium which show an energy penalty for the dimerized chain.

This broad philosophy can be extended to view trends in the periodic table in general. If electronegativity is regarded as a weighted sum of atomic orbital ionization energies, then this is an index which scales with the driving force for distortion and thus is a very useful indication of the occurrence of metallic character. Indeed there are quantitative measures of the concept "metallicity", in terms of the values of the atomic energy levels of the constituents.

The discussion above emphasizes the need to remove from the vernacular the traditional concept of the metallic bond. Metals of the type described above are just those systems, usually well-described by the orbital model, but where the driving force is not large enough to open a gap at the Fermi level. An area where the traditional view of the metallic bond is especially inappropriate is that of the molecular metals, often based on completely "organic" compounds. These are simply systems, held together by van der Waals forces, where there is a small but important overlap between the orbitals of each unit to form energy bands. On doping by either intrinsic or extrinsic means, these bands may become partially filled and metallic conduction possible. The electronic description of these materials is readily accessible by tight-binding calculations.

There are many examples of solids, however, where although the structure is distorted away from a parent and localized bonds readily envisaged, the material is still metallic. These are the metalloids, antimony and bismuth being typical examples. On descending this group of the periodic table, the ratio of "bonded" to "nonbonded" distances becomes closer to unity. As a result of the significant interaction of adjacent sheets imposed by these short nonbonded distances, there is some overlap between highest occupied and lowest unoccupied bands. Within the present model the metalloids are just those systems where the driving force is not quite large enought to open a gap. The phrase "metalloid bonding", sometimes used to describe this state of affairs, ought to be removed from usage, too.

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(16) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

(17) Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1952**, *20*, 837.