The Metallic Bond-Dead or Alive?
Kommentar und Antwort

Comment by Leland C. Allen* and Jeremy K. Burdett*

In a recent 'Highlight' J. C. Schön discussed[1] a point of view put forward by ourselves[2,3] that the term 'Metallic Bond' should be dropped from the chemical vernacular. Although Dr. Schön gives a useful summary of the thrust of our work, his conclusions are the opposite to ours—the metallic bond is alive and well, he believes, as a distinct entity on a par with the ionic, van der Waals, and covalent bonds which chemists use to categorize compounds. There are some other points that support our view, which are worth stating here. We will show once again that 'metallic bonds' are a subset of that large group of bonds we loosely call 'covalent'.

1) To estimate the strength of ionic interactions, one would use an interatomic potential of the form $-e^2/r + A/r^6$, where the electrostatic interaction is balanced by a repulsive term. This approach has been used for years to estimate the cohesive energies of ionic materials. To estimate the strength of van der Waals interactions we would use a potential of the form of $-B/r^6 + C/r^{12}$, the age-old Lennard-Jones 6-12 potential. To estimate the strength of covalent bonding we would try to evaluate the integral $\int \phi_1 H^{\mathrm{eff}} \phi_2 \mathrm{d}\tau$, or use empirical expressions to access these overlap terms. But what do we use to estimate the strength of 'metallic bonding'? What is the special electronic characteristic that distinguishes it from the other three types? In fact, we use the same considerations as for covalent bonding. Tight-binding theory used in the solid state, for metals as well as insulators, is just like the Hückel theory of the organic chemist.[4] The use of the terms 'ionic', 'covalent', and van der Waals, are of course frequently imprecise, but in a perfectly accurate electronic structure calculation, all of these considerations are included. Importantly no special theory is included for the 'metallic' bond.

2) Energy differences between the bcc, fcc, and hcp crystal structures of the transition elements[5,6] as a function of electron count may readily be calculated, and thus the most stable structure identified. Excellent agreement with the observed structures is found. These particular calculations[5,6] used tight-binding theory—as we pointed out in (1), the solid state analog of molecular orbital theory. No special 'metallic bonding' was used to get these results—just orbital overlap considerations. Thus the crystal structures, and indeed their cohesive energies, are determined by d-band covalency. The Hume-Rothery electron compounds, often very complex crystal structures that are found for metallic alloys with between 11 and 12 valence electrons per atom are also completely accessible[7] using this solid-state equivalent of Hückel theory. Again no special 'metallic bonding' needs to be implied.

3) Pauling[8] regarded metals as really no different from large molecules where there are not enough electrons to form electron pair bonds between all close atomic contacts. He used the concept of resonance to get over this problem, just as he used resonance to view the electronic structure of the π manifold of benzene. His Resonating Valence Bond model certainly has an appeal, and has recently found new uses in the physics community. Thus, as pointed out in our paper,[2] and hardly a new observation, there are strong similarities between the electronic descriptions of metallic solids and molecules with delocalized electrons such as benzene.

4) Important in this regard too are aspects of the van Arkel-Ketelaar diagram.[3] The electronic underpinnings of the scheme come from 'covalent' arguments. Particularly interesting, is the reduction of a three variable scheme (the original triangle itself, with 'ionic', 'covalent' and 'metallic' bonding variables) to a two variable scheme,[3] essentially 'ionic' and 'covalent' indices.

In view of these comments, which surely put the electronic structures of metals within the same electronic framework as the 'covalent' bond, our argument stands, that the 'metallic bond' as a separate term with equal weight to the other three traditional schemes should be abandoned. Certainly it does not have a mathematical framework distinct from the other three categories as shown in (1) above. However, if one wishes to use the term to describe that subset of 'covalent' systems, which are metals then one should be aware of the discussion above.

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