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Multiple Metal–Metal Bonding and *A*-Chain Integrity in Superconducting A_3B (β-Tungsten) Alloy*

YING-NAN CHIU†,‡ AND FREDERICK E. WANG‡
†Department of Chemistry, The Catholic University of America, Washington, D.C. 20064, and ‡Innovative Technology International, Inc., 10747-3 Tucker Street, Beltsville, Maryland 20705

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Charge overlap and molecular orbital energies for the $-(M_2)-$ linear chain unit are computed for selected transition metals. For valid comparison, uniform parameters are used starting with the type of d^nsp excited configuration of the atoms that is favorable to linear digonal hybrid bonding. Stabilities of the chains are then compared. Bond order and bond energies of σ, π, and δ bonds for the *d* molecular orbitals are deduced. Results support the existence of linear chains of group V or group VI atoms as the *A* atoms in superconducting A_3B alloys. Conjugated resonance structures are drawn for all multiple bonds in the chains. A possible relationship between chain integrity (and conjugation) and conductivity in such alloys is suggested.

I. Introduction

Ia. Statement of Objectives and Experimental Background for A-Chain Integrity

Since Weger (*1*) concluded the importance of "*A*-chain integrity" in yielding favorable superconducting characteristics, there has been experimental and indirect theoretical support for the existence of a strongly bonded *A* chain. The purpose of this work is to determine the nature of *A*-chain bonding in relation to multiple covalent bonds and to explore its implications in superconductivity.

To justify our emphasis on *A* atoms while neglecting *B* atoms, we enumerate the experimental evidence below. (i) Staudemann *et al.* (*2*) in their X-ray diffraction studies of superconducting V_3Si, showed unusually high electron charge concentration between V atoms within the infinite chain. Subsequent work (*3*) on nonsuperconducting Cr_3Si also showed a similar tendency (although to a lesser degree). (ii) The positron annihilation experiment (*4*) on V_3Si demonstrated this linear chain of V atoms. (iii) The microhardness experiment of Chin *et al.* (*5*) pointed to strong covalent-like bonds in the *A* chains.

The linear chain model received general theoretical support in the tight *d*-band study of V_3Si compound (*6*) and other transition metals (*7*). Although in pure metals Nb and Al have the same metallic radii (1.43 Å), in Nb_3Al the Nb–Nb distance of 2.59 Å is much shorter than the expected Nb–Al distance of 2.89 Å, indicating predominant *A–A* rather than *A–B* interaction. This

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trend of shorter A–A interatomic distance persists in other A_3B compounds. The relevance of this predominant A–A bond to superconductivity has been proposed by Schoijet (*9*). A general review of A-chain integrity is available (*10*).

Aside from the direct evidence mentioned above, there is indirect evidence which supports the A-chain importance. The phase diagram correlation study of Wang (*11*) showed that A can substitute for B but B cannot replace A (atom). It has been shown that substitution of B with B' does not adversely affect the superconducting critical temperature, T_c. However, substitution of A with A' led to a collapse of the "A-chain integrity" and resulted in lowering of T_c. Order and disorder parameter analysis (*13*) demonstrated that preferential disorder appeared in the B site leaving A-site integrity intact. While the X-ray analysis showed some charge transfer (2) from the Si atom to V atom in V_3Si, the end effect of the charge transfer led to a strengthening of the A chain. Our molecular-orbital analysis demonstrates transferred electrons to go to the bonding δg orbital of the $-V_2-$ chain configuration (see Section II below).

Ib. The Question of Multiple Bonding in Superconducting A_3B Compounds

Our purpose is to establish the theoretical basis for multiple covalent bonds in the A chain and to correlate the propensity of multiple bonds with the property of superconductivity in A_3B compounds.

With the discovery of quadruple bonds (*14*) (between Re atoms) in transition metal complexes, interest has been generated in the metal–metal bonds. Notably, those in the complexes of V, Cr, Mo, and W have been discovered and studied (*15–22*). Multiple bonds are well recognized in dimetal complexes and metal complex clusters of up to M_6, as evident from Cotton's review (22). However, in the review there is no mention of linear chains of metals nor of A_3B compounds. In the discussion (*23*) of the "A-chain integrity," Wang and Mitchell noted the peculiarity of having the same type of elements (V, Cr, Nb, Mo, W, etc.) serving as the A atoms in A_3B compounds. It is interesting to note that precisely the same type of elements are found (*22*) to be multiply bonded in their complexes. This led us to ponder about the possibility of multiple bonds in the "A chain" and subsequently the effect of multiple bonds and conjugation on superconductivity.

Ic. Conjugation of Multiple Bonds and the Superconducting Mechanism.

Our purpose is to demonstrate the conjugation of multiple A–A bonds in A_3B compounds by drawing the resonance structures, and to discuss its connection to superconductivity. In the case of conjugate carbon–carbon bonds in annulenes, Haddon (*24*) not only computed the ring currents but also analyzed the lack of integrity of knowledge on nondissipative currents in organic molecules and bulk superconductors. Common facets of present theories associated with annulenes were also discussed by the author.

In 1976, following Wang's "Covalon" model, the present authors (*25, 26*) used a double harmonic oscillator treatment (*27*) in proposing a pairwise hopping model for the phonon-coupled electron transfer along a covalently bonded, conjugated linear chain of atoms. This covalent aspect of conductivity is corroborated by Krüger's idea of quasi-orbital electrons in superconductivity (*28, 29*). However, neither Krüger nor other authors (*2, 3, 9*) have considered a conjugated chain of metal atoms. We, therefore, feel it is useful to find bond alternation in multiply bonded A-chain structures in which the antisymmetric vibration will help move the short bond with more bonding electrons (viz., from A–A—A to A—A–A). While this may not be the only mechanism for conduction, it should provide another link to our ultimate understanding of the superconducting mechanism. Furthermore, it is a good example of antisymmetric phonon-coupled interaction of a pair of electrons which behaves as bosons. It should be noted there has been great interest (*30–32*) in one-dimensional linear chain metal compounds with anomalous conductivity characteristics. However, the emphasis appears to be on mixed-valence compounds. These compounds reduce the on-site Coulomb repulsion (during charge pileup) which creates a barrier for charge fluctuation. In the multiple-bond conjugation model a pair of bonded electrons can move through conjugation to a neighboring bond without violating Pauli's exclusion principle or without piling up in excited high-energy orbitals at the same atomic site (thus increasing Coulomb repulsion).

Connected with the purposes mentioned in Ia, Ib, and Ic, there are two major theoretical questions: (i) What is the relative possibility of linear chain formation among different atoms and different transition series? (ii) What are the multiple bond possibilities and how will these bonds conjugate along a chain?

To answer these questions, we made a comparative study of selected elements from the three transition metal series (question (i)). Using the results of this study, we drew resonance structures for a chain of metal atoms and discussed their implications (question (ii)).

II. Charge Overlap Computation and Molecular Orbital Calculation for a Repeating Unit $-(M_2)-$

For the purpose of comparison of different metals among and between different series, the philosophy of calculation here strives for maximum internal self-consistency. We consider the same repeating unit $-(M_2)-$ for all metals and impose the same d^nsp configuration for all elements. This is the atomic configuration favorable to *dp* or *sp* digonal hybrid bonding in a linear chain. We use the rule of Burns (*33*) to generate all single-ζ Slater orbital exponents and use them to compute σ, π, and δ overlaps between the appropriate *s*, *p*, and *d* orbitals at several interatomic distances of interest. The magnitudes of these overlaps for all three series are shown in Fig. 1, where their relative magnitudes may be compared. The relatively large size of the P_π and P_σ overlaps (and the *S* overlaps) prove the correctness of the choice of the d^nsp configuration and the importance of *dp* and *sp* hybridization.

Using these overlap integrals, we employ an extended Hückel theory (*34*) to compute the molecular orbitals for these $-(M_2)-$ units. The purpose is to find relative bonding energies and to see if the resulting stabilization is sufficient to compensate for the energy exciting to the d^nsp configuration. The answer is affirmative except for some doubt in the cases of Y and Zr. The favorable bonding situation of $-(V_2)-$ is illustrated in Fig. 2. This result comes from molecular orbital calculations using the Mulliken–Wolfsberg–Helmholz approximation (*35, 36*). With this approximation, the Coulomb integral is equated to the valence orbital ionization energies while letting the resonance integral be proportional to the overlap and Coulomb integrals, i.e., $H_{ab} = K(\frac{1}{2})S\,(H_{aa} + H_{bb})$. The same parameter, $K = 1.75$, is used throughout the transition metal series. The same sets of Hartree–Fock self-consistent field atomic energy calculation (*37, 38*) were used to compute the valence orbital ionization potentials and excited d^nsp configuration energies.

The resulting molecular orbitals show $\sigma_g nd$, $\pi_u nd$, and $\delta_g nd$ to be the lowest bonding molecular orbitals, confirming earlier predictions (*39*) of the importance of *d*-bonding in such metals. The molecular orbital (M.O.) configuration in the case of

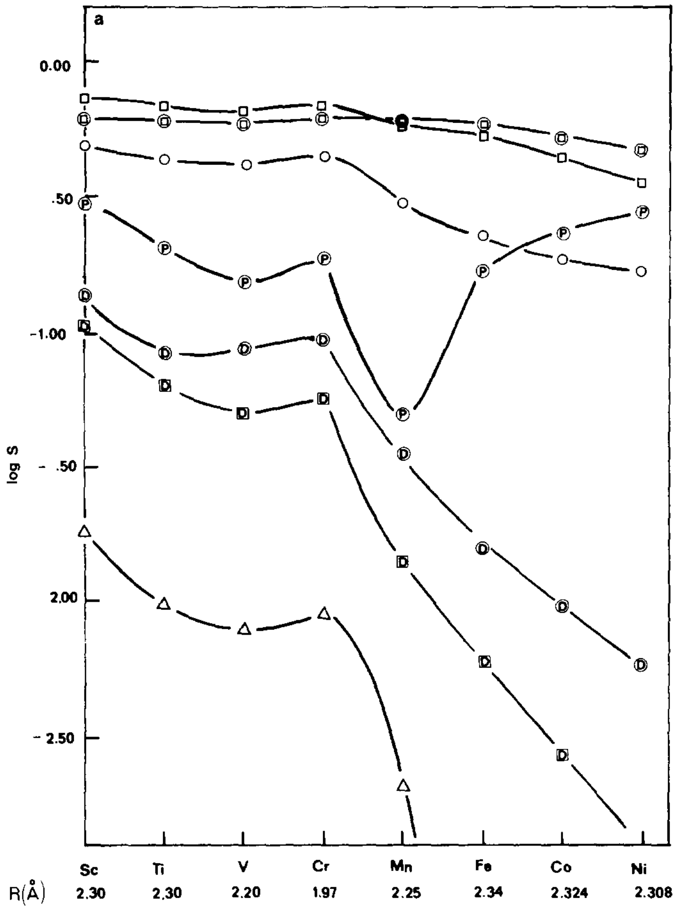

FIG. 1. Logarithm (base 10) of selected charge overlaps vs selected radii of transition elements. (a) First transition series; (b) second transition series; (c) third transition series. ○, for $S(ss)$; Ⓟ,. for $S(p\sigma p\sigma)$; □, for $(p\pi p\pi)$; ⊡, for $S(sp\sigma)$; Ⓓ, for $s(d_\sigma d_\sigma)$: $\boxed{\text{D}}$, for $s(d\pi d\pi)$; △, for $S(d\delta d\delta)$. To avoid overcrowding the following overlaps are not plotted: $S(sd\delta)$; $S(p\pi d\pi)$; $S(p\sigma d\sigma)$.

–(V_2)– is $(\sigma_g 3d)^2(\pi_u 3d)^4(\delta_g 3d)^2 + (\sigma_g 3d)^2$, where the last two electrons in $\sigma_g 3d$ are reserved for σ-bonding to the two neighboring units in the linear chain. The energy in Fig. 2 includes these two electrons in a chain unit. If we exclude these two electrons we obtain the bonding stabilization energy between two atoms only. The stabilization energy given in Figs. 3 and 4 reflects the difference between the M.O. energies and the atoms after nuclear repulsion is taken into account and excitation energy compensated. For –(V_2)–, it is for the interatomic distance $R_2 = 2.35$ Å found in A_3B compounds. Aside from these σ bonds to neighbors, the configuration gives one σ, two π, and one σ bond, or a maximum bond order of 4. However, if the π and δ bonds have resonance conjugation over the infinite chain, on the average between each pair of neighboring metal atoms there will be only one σ, one π, one-half δ bond or an average bond order of 2.5. Similar analysis and the average bond orders for other metals in the first and second transition series are given in Fig. 5. We solve for the energy of σ, π, and δ bonds by using the ratio of the relative stabilization of the

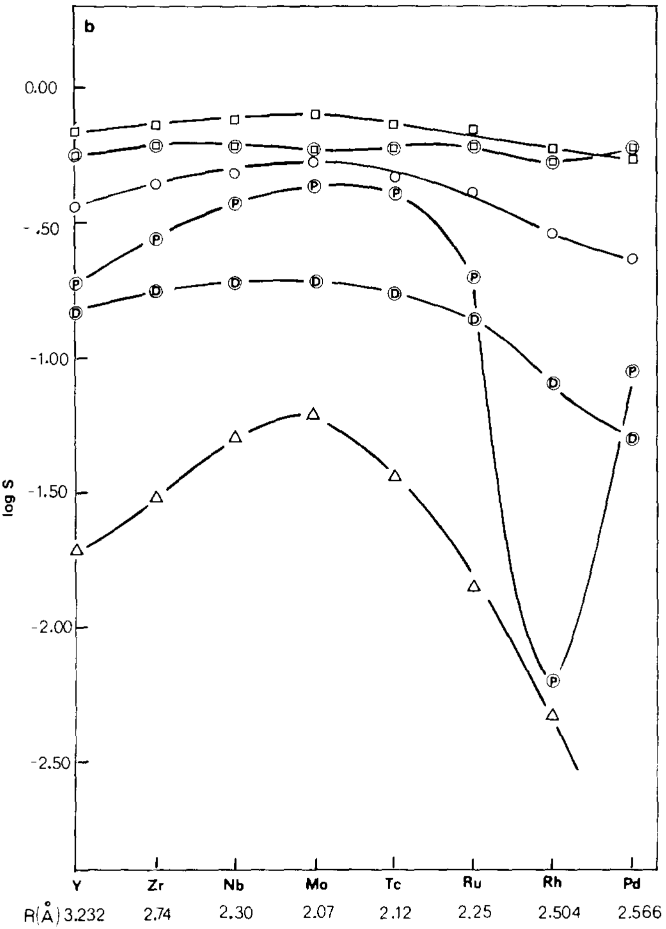

FIG. 1—*Continued.*

$\sigma_g nd$, $\pi_u nd$, and $\delta_g nd$ molecular orbitals compared with atomic nd orbital. It is based on these energies that the average bonding stabilization energies for the metals in the first and second series and for the interatomic distances of interest are given in Figs. 3 and 4. Details of this calculation are given in a separate paper (*40*). The theoretical basis for calculating bonding stabilization is given in the appendix of that paper. The molecular orbitals for some elements (Rh and Pd in the second series and all of the third series) are not calculated for comparison, because comparable self-consistent sets of valence orbital ionization potentials and configuration energies are not available. However, charge overlaps are calculated (Fig. 1) and qualitative trends are deduced. Note that the configuration energies for the third series are lower (*40*) even though the overlaps are comparable to the preceding series. Therefore, multiple bonding in the third series is probable. Actual cases for W and Re are, of course, well known (*16–22*).

The average stabilization energy of 2.68 eV obtained (at R = 2.44 Å) for the $-(V_2)-$ chain unit is accidentally close to the dissociation energy of 2.46 eV for the not-exactly-comparable isolated V_2 molecule (*41*). The maximum stabilization energy obtained for a larger bond order (4 vs 2.5) and

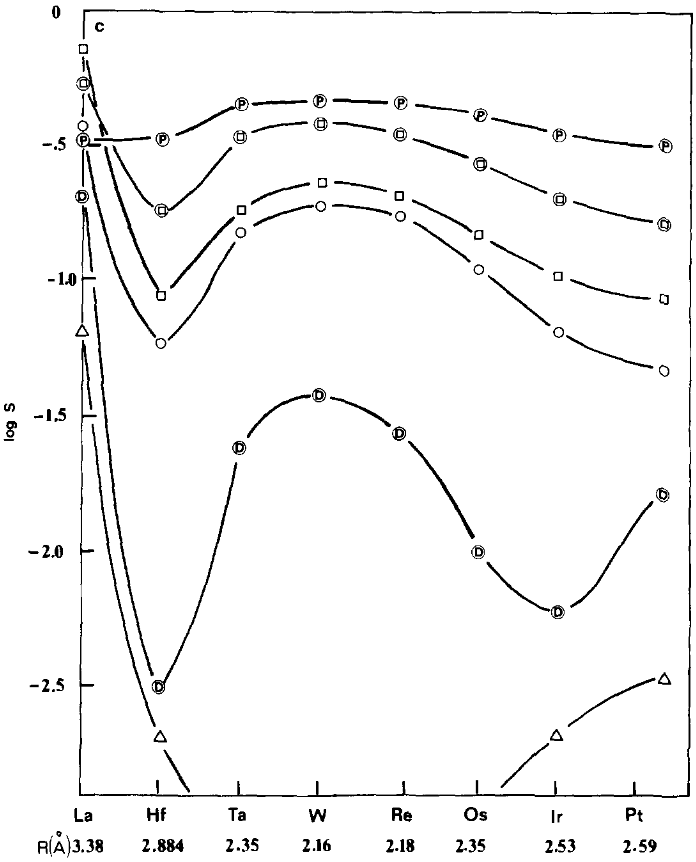

Fig. 1—*Continued.*

shorter distance (R = 2.20 Å) is 4.68 eV. The stabilization for the chain unit should be larger because of lessened electron repulsion in chain formation and because of resonance conjugation (see next section). For the –(Nb_2)– chain unit the average stabilization is 8.26 eV compared with 5.21 eV for the free Nb_2 molecule.

III. Resonance Conjugation of Multiple Metal–Metal Bonds

From molecular orbital calculations we know that multiple d-bonding exists between metals in the –(M_2)– chain unit. The molecular-orbital bonding energies are compared to atomic d orbital energies (H_{dd}) in Fig. 6. The average bond orders, with the multiple bonds evenly spread out along the chain, are given in Fig. 5. However, in a resonance conjugation there are many ways to write resonance structures, corresponding to the spread from maximum bond order between the two metal atoms. However, because of the degeneracy of M.O. energies and the occurrence of open shell structures, care must be exercised to recognize resonance structures with different azimuthal angular momentum and spin angular momentum. Resonance structures for the same number and type of bonds are the same. Chain structures for group III (Sc max. two bonds), group IV (Ti max three bonds), group V (Nb max four bonds), and group VI (Mo max. five bonds) are shown in Figs. 7–10. All included resonance struc-

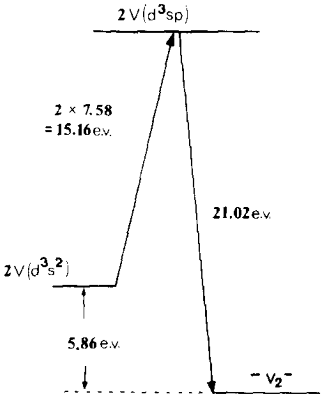

FIG. 2. Excitation of two ground-state vandium atoms (in d^3s^2 configuration) to d^3sp configuration and subsequent stabilization in forming a repeating unit $-(V_2)-$ in a linear chain. Expenditure of excitation energy here is more than compensated by bonding stabilization. The maximum net bonding within the unit and between the two V atoms (excluding bonding to the two neighboring units) has an energy of 3.95 eV corresponding to one σ, two π, and one δ bonds.

tures are consistent with the translational symmetry of the diatomic $-(M_2)-$ unit. Other resonance structures are possible, but they require studies of triatomic chain units or larger. These studies may not be needed because experimental indications of alternate short and long bonds can be explained in terms of diatomic units $-(M_2)-$. Also larger units would mean that π or δ electrons of the same symmetry are too far apart to undergo conjugation. In Fig. 11, we show only four atoms or two units. Examples of the spin and angular momenta of the individual and combined units are indicated. Average bonding corresponds to structures of the same number of bonds between any two neighboring atoms. It is clear that there are many structures with different numbers of bonds between the atoms. For example, in Fig. 8 the $-(Nb_2)-$ similar to $-(V_2)-$ has a maximum of four bonds ($\sigma + 2\pi + \delta$) between two neighboring atoms. Structures *f* and *g* (to the right) have the same number of bonds between each neighbor. If we consider only those eight structures with full (two-electron paired) bonds (Fig. 9, lines a, b, c, d), the average number of bonds between atoms *i* and *j* are:

ij	σ bond	π bond	δ bond	total
(*12*) or (*34*)	1	1.5	0.5	3.0
(*23*)	1	0.5	0.5	2.0

This shows a clear difference of bond numbers (or bond orders) and hence bond lengths. Even if these were complete delocalization of the bonds, giving averaged bonding structures such as those on the

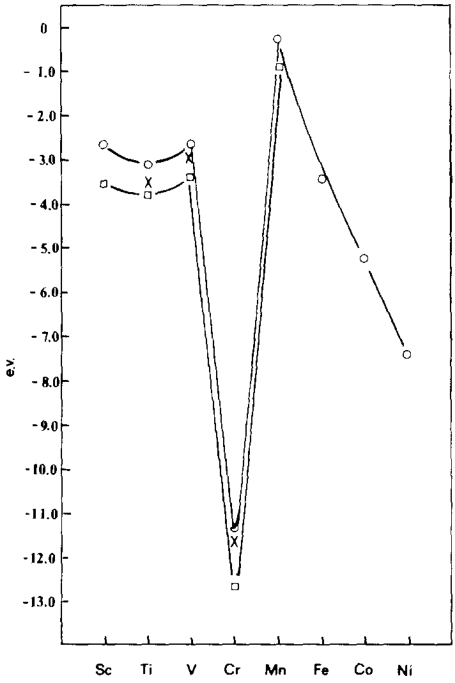

FIG. 3. Average bond stabilization between two first-series transition metal atoms in a linear chain: O for R_1 metallic distance of Pauling; × for R_2, distance in A_3B compounds Ti(2.50), V(2.35), Cr(2.34); □ for R_3, short distance for multiple metal–metal bonding in some complexes, Sc(2.30), Ti(2.30), V(2.20), Cr(1.97), Mn(2.25), some R_3 by extrapolation. All are in angstroms. For V see F. A. Cotton and M. Miller, *J. Amer. Chem. Soc.* **99**, 7886 (1977); for Cr see F. A. Cotton, *Acc. Chem. Res.* **11**, 225 (1978); for Sc see R. Busby, W. Klotzbucher, and G. A. Ozin, *J. Amer. Chem. Soc.* **98**, 4013 (1976).

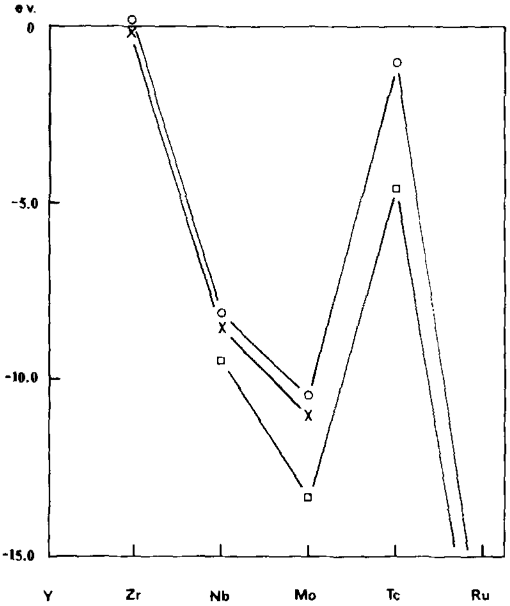

FIG. 4. Average bond stabilization between two second-series transition metal atoms in a linear chain. ○ for R_1 distance of Pauling; X for R_2, distance in A_3B compounds, Zr(2.74), Nb(2.56), Mo(2.46); □ for R_3, short distances for multiple metal–metal bonding in some complexes, Nb(2.30), Mo(2.07), Tc(2.12), Ru(2.25). Some R_3's are by extrapolation. All are in angstroms. For Mo see F. A. Cotton *et al.*, *J. Amer. Chem. Soc.* **100**, 4725 (1978); for Tc and Ru see J. L. Templeton, *Prog. Inorg. Chem.* **26**, 211 (1979).

right side of lines e and f, the pseudo-Jahn–Teller effect (*42*) would cause distortion into alternating short and long bonds.

The above calculations would support the bond alternation (*43*) in the A-chain atoms of A_3B compounds during martensitic transitions at low temperature. In principle, all of the doubly degenerate $d\pi_{xz}$, $d\pi_{yz}$, $d\delta_{xy}$, and $d\delta_{x^2-y^2}$ orbitals are mutually independent and orthogonal and each will resonate along the infinite chain. This is different from the finite-length cumulenes for which end effects are important and for which the bonds are assumed equal in the first-order molecular-orbital treatment.

In our case, consider alternating π bonds—the same applies to δ bonds. If we take the resonance integrals for the long and short bonds to be β_1 and β_2, respectively, conjugation over a chain of $2N$ such metal atoms would yield a molecular-orbital energy (*42*, *44*)

$$\epsilon_j = \pm\left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos \frac{2j\pi}{2N+1}\right]^{1/2}, \qquad j = 1, 2, \ldots . N, \quad (1)$$

which reduces, for equal bond lengths and $\beta_1 = \beta_2 = \beta$, to

$$\epsilon_j = 2\beta \cos\left[\frac{j\pi}{2N+1}\right], \qquad j = 1, 2, \ldots . \; N. \quad (2)$$

To determine the energy gain due to resonance conjugation over the chain, we define the root-mean-square energy of N doubly occupied orbitals as (per electron)

$$[\epsilon^2]^{1/2} = \left[\frac{1}{2N}\sum_{j=1}^{N} 2(\epsilon_j)^2\right]^{1/2}. \quad (3)$$

We then substitute the energy expression from Eq. (1) and for large N define the variable $X = 2\,j/2N + 1$ and change the sum integral form as follows:

$$[\epsilon^2]^{1/2} = \left[\frac{1}{2N}\,2\,\frac{2N+1}{2}\int_{2\pi/2N+1}^{\frac{2\pi N}{2N+1}} (\beta_2^1 + \beta_1^2 + 2\beta_1\beta_2 \cos x)dx\right]^{1/2} = (\beta_1^2 + \beta_2^2)^{1/2}. \quad (4)$$

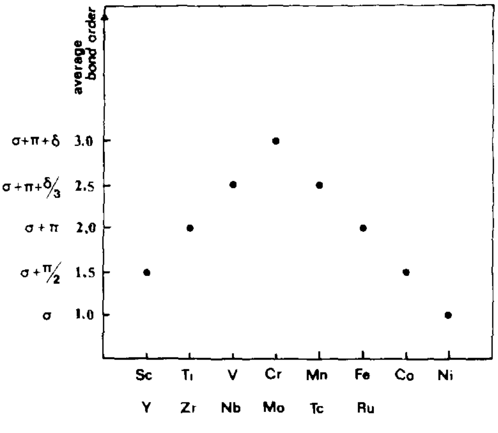

FIG. 5. Average bond order between neighboring transition atoms in a linear chain.

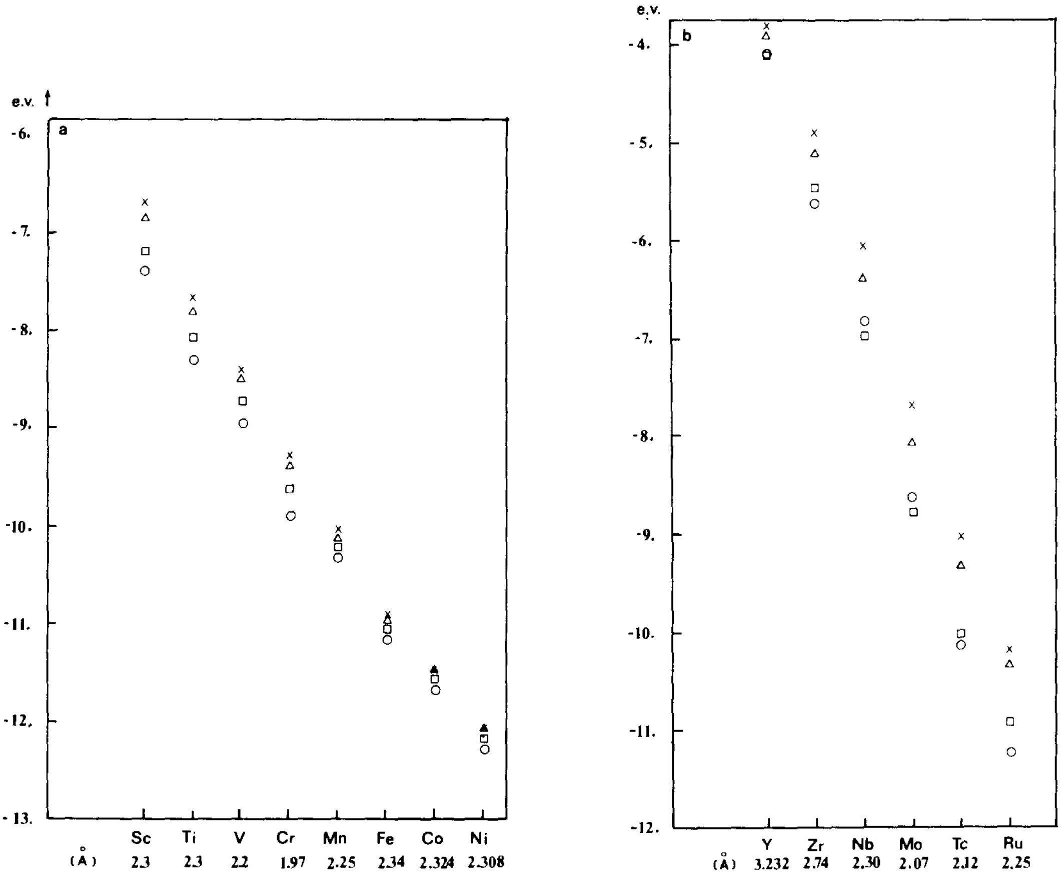

FIG. 6. Bonding d-molecular orbital energies of the transition metal chain unit $-(M_2)-$. Figure shows the general magnitude of the splitting due to σ, π, and δ interaction within a unit. The distances between metal atoms are given under each atom. Only the shortest distances studied are shown. Therefore, the relative splitting of energies is not to be taken as a trend for the series. The d-atomic orbital energies given are simple $-H_{dd} \cong d$-VOIE for the d^nsp excited configuration which was used to construct the molecular overlap and molecular orbitals. ×, $-H_{dd}$; △, $\delta_g 3d$; □, $\pi_u 3d$; ○, $\sigma_g 3d$.

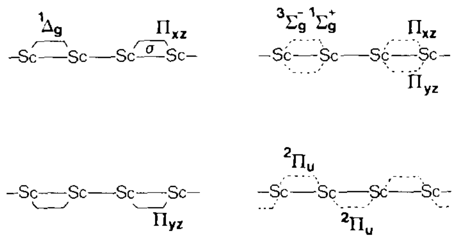

FIG. 7. Conjugate structures of the $[-Sc_2]_n$ linear chain; the maximum bond order is two (σ, π). Same structure for $(-Co_2-)_n$. Straight line for σ, bracket for π bond. Broken line for singly occupied bonding orbital or one-electron bond.

For $\beta_1 = \beta_2$ the root-mean-square energy is $\sqrt{2}\beta = 1.41\beta$. This is to be compared with the isolated, nonresonant, and unconjuga-

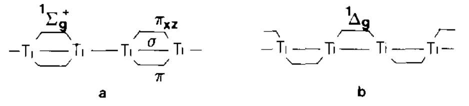

FIG. 8. Conjugate structures of the $(-Ti_2-)_n$ linear chain; the maximum bond order is three (σ, 2π). Same structure for $(-Fe_2-)_n$ and $(-Ru_2-)_n$.

ted case for which each bond has $\epsilon_j = \beta$ and the root-mean-square energy is β. Therefore there is a resonance gain of about 40% of the root-mean-square energy for each electron. For the case of equal bonds for which the energy per se (Eq. (2)) rather than the square of the energy can be integrated to get the average, the gain in average energy (*40*) is 27%. With this kind of resonance gain in energy, the destabilized case of Y or Zr (Fig. 4) may become more stabilized. However, one complication is the possible overlap of σ, π, and δ bonding bands. Inspection of Eq. (2) shows that the maximum spread of resonance energy is large, i.e., $4\beta = 2\beta - (-2\beta)$, corresponding to $\cos(0)$ and $\cos(\pi)$ (vs the one-bond energy spread of 2β). This overlap may be further complicated by the larger gap between bonding and antibonding long-chain molecular orbitals that appears when the bonds have alternating lengths. To wit, Eq. (1) shows that the highest chain orbital bonding energy (corresponding to $j = N$) is $-\left[\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\frac{2N\pi}{2N+1}\right]^{1/2}$, whereas the lowest antibonding orbital energy has the same magnitude but opposite (positive) sign. Normally, molecular orbitals of lower (e.g., π_u is lower than δ_g) energy in the $-(M_2)-$ units are filled first, when each orbital character is distinct; however, when overlap occurs there will be bonds of mixed π and δ character. These complications will not be treated in this work. As a first step, we try to understand the possible and simultaneous existence of σ, π, and δ bonds in a chain. Suffice to say that the overlap of the bands and band theory may be invoked to explain different bonding characteristics from that found in the simple $-(M_2)-$ unit. We have also used simple molecular-orbital theory for chemical insight into bonding, partly because molecular orbitals in a chain (as treated by Eqs. (1) or (2)) will have the appropriate phase factors which would fa-

TABLE Ia

MAXIMUM σ, π, AND δ BOND STRENGTHS IN $-M_2-$ CHAIN UNIT AND ESTIMATED FORCE CONSTANTS

	Sc	Ti	V	Cr	Mn
R (Å)	2.30	2.30	2.20	1.97	2.25
σ bond (eV)	2.61	2.39	2.06	7.31	0.29
π bond (eV)	1.90	1.48	1.21	4.50	0.11
δ bond (eV)	0.37	0.26	0.20	0.73	0.01
Max. bond order	2(σ, π)	3(σ, 2π)	4(σ, 2π, δ)	5(σ, 2π, 2δ)	4(σ, 2π, δ)
Max. est k^a	1.6×10^4	2.6×10^4	3.0×10^4	4.3×10^4	1.3×10^4 dyne/cm
Max. est. ω_e (cm^{-1})	109	134	141	167	90
Ave. bond order	1.5(σ, π/2)	2(σ, π)	2.5(σ, π, δ/2)	3(σ, π, δ)	2.5(σ, π, δ/2)
Ave. est. k	1.0×10^4	1.6×10^4	1.8×10^4	2.1×10^4	1.0×10^4 dyne/cm
Ave. est. ω_e (cm^{-1})	88.0	105	110	115	80
Exp. free $M_2{}^b$ ω_e (cm^{-1})	230	288	325	400	van der Waals molecule
R_e (Å)	2.5	2.5	2.32	2.22	

[a] Slope = kx (eV/Å); k = slope/x; x = 2.35 Å for all; eV/Å^2 = 1.602×10^4 dyne/cm. $\omega_e = \frac{1}{2c}\sqrt{\frac{k}{u}}$. This is a very rough estimate. Only the relative size and trend (of increase and decrease) with respect to other elements in the series and the trend with respect to the bond order change of the same element chain unit are meaningful.

[b] Cited by W. F. Cooper, G. A. Clarke, and C. R. Hare, *J. Phys. Chem.* **76**, 2268 (1972).

TABLE Ib

MAXIMUM σ, π, AND δ BOND STRENGTHS IN $-M_2-$ CHAIN UNIT AND ESTIMATED FORCE CONSTANTS

	Nb	Mo	Tc	Ru
R (Å)	2.30	2.07	2.12	2.25
σ bond (eV)	3.95	4.77	2.29	9.97
π bond (eV)	4.30	5.77	2.20	7.21
δ bond (eV)[c]	1.23	1.72	0.54	1.31
Max. bond order	4(σ, 2π, δ)	5(σ, 2π, 2δ)	4(σ, 2π, δ)	3(σ, 2π)
Max. est. k[a]	4.1×10^4	6.2×10^4	4.9×10^4	6.6×10^4 dyne/cm
Max. est. ω_e (cm^{-1})	121	147	130	148
Ave. bond order	2.5(σ, π, δ/2)	3(σ, π, δ)	2.5(σ, π, δ/2)	2(σ, π)
Ave. est. k	1.5×10^4	2.5×10^4	2.8×10^4	2.8×10^4 dyne/cm
Ave. est. ω_e (cm^{-1})	74.6	94.7	99.4	97.5
Exp. M_2 complex ω_e (cm^{-1})		477[b]		
R_e (Å)		1.929[b]		
Bond order		6		

[a] Slope = kx (eV/Å); k = slope/x; x = 2.4 Å for all; eV/Å^2 = 1.602×10^4 dyne/cm.

[b] B. E. Bursten, A. Cotton, and M. B. Hall, *J. Amer. Chem. Soc.* **102**, 6349 (1980).

[c] δ bond was estimated to be 20 kcal in MO_2X_6 by Trogler and Gray (Ref. (*17*)).

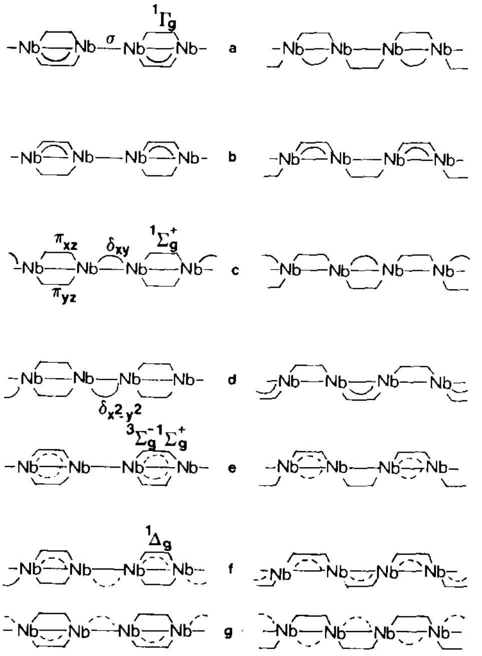

FIG. 9. Conjugate structures of the $(-Nb_2-)_n$ linear chain; the maximum bond order is four. Same structure for $(-V_2-)_n$, $(-Mn_2-)_n$, $(-Tc_2-)_n$. Straight line for σ, bracket for π, and curve for δ bond. Broken line for singly occupied bonding orbitals or one-electron bonds.

cilitate the application of Woodward–Hoffmann rules (*45*) in reactions involving finite metal chains as catalysts.

IV. Discussion

From charge overlap and bond stabilization, we deduce the reason for the integrity

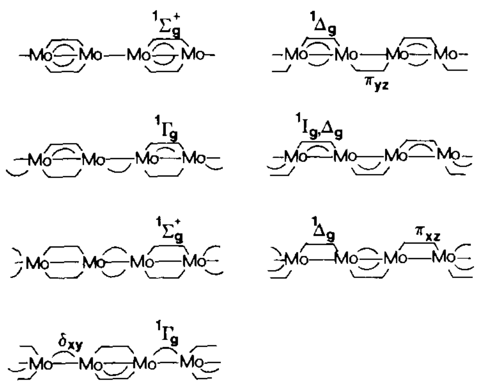

FIG. 10. Conjugate structures of the $(-Mo_2-)_n$ linear chain; the maximum bond order is five. Same structure for $(-Cr_2-)_n$.

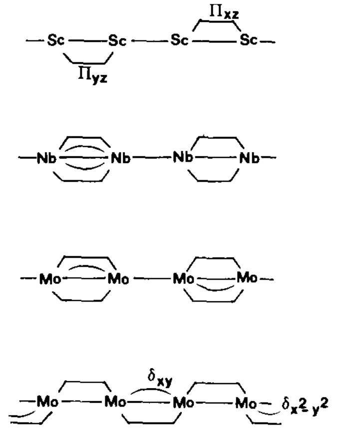

FIG. 11. Structures that hinder conjugation. Note that π_{yz} does not conjugate with π_{xz}. The next π_{yz} electrons are too distant (three bonds away). Same may be said about the δ_{xy} electrons relative to the $\delta_{x^2-y^2}$ electrons of Mo. But the detrimental effect of the π electrons, forming a stronger bond, should be greater. A structure of Nb which requires four atoms for a repeat unit also shows that the δ electrons are too distant (three bonds away) for conjugation. Complete π conjugation may compensate for lack of δ conjugation.

of stable linear chains of transition metal atoms. From the nature of *d*-orbital bonding, we deduce resonance conjugate structures of the chain and the possibility of bond alternation. The case is clear-cut for group VI elements (Cr and Mo) with the largest stabilization energies (Figs. 3 and 4), highest bond orders (Fig. 5), and largest numbers of resonance conjugate structures. This ensures linear integrity (instead of bent or zig-zag structures) as found in –(Sc)– due to preferential occupation of one of the degenerate $d\pi_{xz}$ or $d\pi_{yz}$ orbitals following the Renner–Teller Effect (*46, 47*). For group V elements (V and Nb), while the stabilization energies are not as great, the number of possible conjugate structures (Fig. 9) is remarkable. This conjugation of bonds should be greatest for Nb and Mo, where π bonds are found to be most prominent (larger overlap and lower energy than the σ bonds). For group VIII elements, such as Fe and Co, stabilization

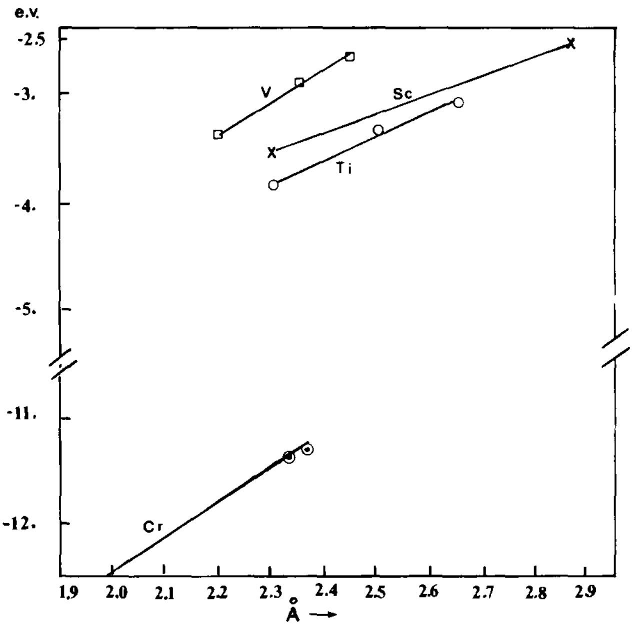

FIG. 12. Improvement of average stabilization energy due to decreasing distance in first-series transition metal chains. The relative size of the slopes (in eV/Å) are Cr(3.08) > V(2.78) > Ti(2.38) > Mn(1.60) > Sc(1.56) at R = 2.30 Å. The "curves" should be segments of parabolas resembling harmonic oscillator potentials.

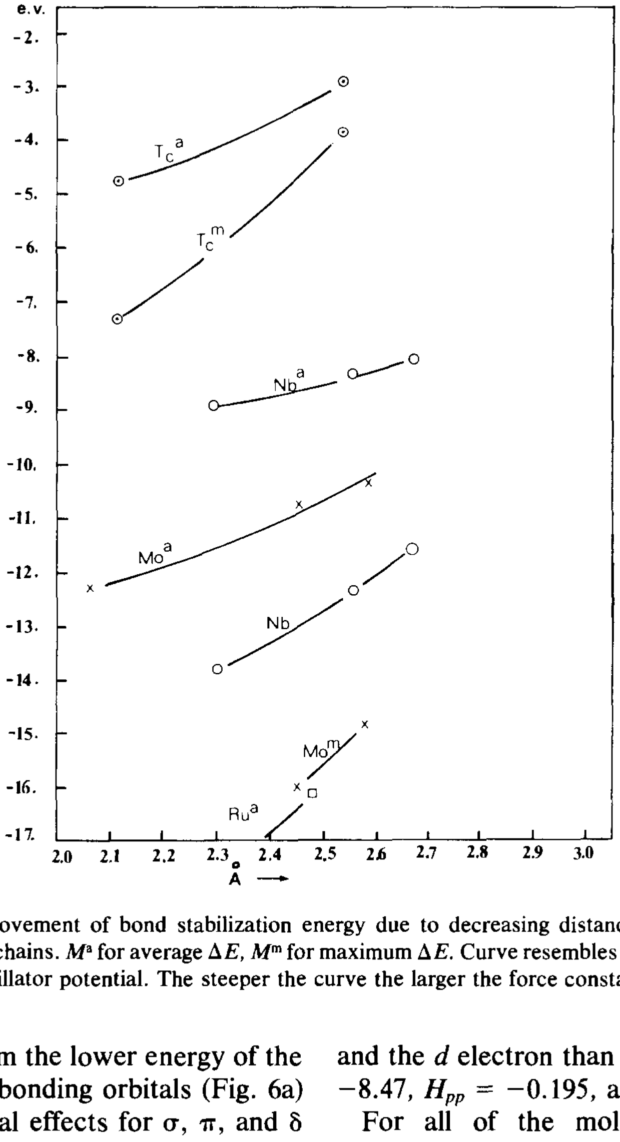

FIG. 13. Improvement of bond stabilization energy due to decreasing distance in second-series transition metal chains. M^a for average ΔE, M^m for maximum ΔE. Curve resembles a parabola segment or harmonic oscillator potential. The steeper the curve the larger the force constant of vibration.

comes mainly from the lower energy of the *d* electrons. The bonding orbitals (Fig. 6a) show only minimal effects for σ, π, and δ bonds. Both δ overlap and δ orbital energy are essentially zero in Co. Thus the overall "bonding stabilization" we computed may contain large Coulomb stabilization of nonbonding electrons rather than resonance stabilization of bonding interaction. This is because we put more of the higher-energy *s* and *p* electrons of the excited configuration into lower-energy *d* molecular orbitals. (For example, in Fe, $H_{dd} = -10.98$, $H_{pp} = -1.68$, and $H_{ss} = -6.20$, there is a greater difference between the *s* and *p* electrons and the *d* electron than in *V*, where $H_{dd} = -8.47$, $H_{pp} = -0.195$, and $H_{ss} = -5.71$.)

For all of the molecular orbitals at the distances chosen the bonding stabilization improves with decreases in interatomic distances. These are plotted in Figs. 12 and 13. If harmonic potentials are assumed, these curves represent a segment of the parabolic potential curve and slopes may be deduced. For the very few points available, a rough estimate (Table I) of slope ($=kx$) yields force constants ($=$slope$/x$) and vibrational frequencies $\left(= \frac{1}{2\pi C}\sqrt{k/\mu}\right)$. These generally increase with multiple bonding and are larger for the known multiply bonded metals V, Cr, Mo, and Ru. The frequencies we estimate for $-(M_2)-$ units are generally smaller than experimental values for the free M_2 molecules (e.g., for V 141 cm^{-1} vs. exp. 325 cm^{-1}). The absolute magnitudes of these frequencies and force constants are not as meaningful as their relative values when comparing chain units of maximum bond order vs average bond order. Thus the force constant 3.0×10^4 dyne/cm for maximum bonding in $-(V_2)-$ vs 1.8×10^4 dyne/cm for average bonding are indicative of the size of the difference for short–long (strong–weak) bond alternation. Thus the more bonding electrons between $-(M_2)-$, the shorter and stronger is the M–M bond. In our earlier work (*3*, *4*) on "Covalon" conduction we suggested that when a pair of bonded electrons moves from a short bond to an adjacent long bond in concert with the change of a long (short) bond to a short (long) bond due to an antisymmetric vibration, a cooperative mechanism of conduction results. In view of the deduced chain integrity of V atoms in superconducting A_3B compounds, we submit that there is a strong possibility of such movement of conjugate electrons along the chain at an appropriate temperature. However, such movement of electron charge alone may not be a sufficient mechanism for superconductivity. We believe that when the movement of charges along one chain induces, through plasmon wave interaction (*48*), movements in neighboring, parallel chains that a self-regenerating and self-sustaining mechanism of superconductivity will result. More work is contemplated along this line.

V. Conclusions

Using a consistent treatment, we computed the s, p, and d orbital overlaps across the transition series, so that rational comparison of trends between the elements may be made. Using these overlaps, we computed molecular orbitals and established the strong d bond between the A atoms in A_3B compounds. It is noted that the compounds with superconducting properties are precisely those especially rich in resonance structure (within the A chain) possessing the possibility of long–short bond alternation along the multiply bonded A chain. The conjugate structures, hitherto not available in literature, are drawn for each element and the average maximum bond orders and energies are estimated. The force constant difference between the long–short bonds are estimated. It is concluded that there is a strong correlation between the propensity to multiple bond formation and the property of superconductivity in these A_3B compounds. Attention is drawn to the similarity of the motion of a bonded electron pair across the alternating long–short bonds by antisymmetric vibration to the phonon-coupled superconductivity.

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