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Superconductivity: small steps towards the “grand unification”

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Abstract The existence of various families of superconducting materials and their T_C values are qualitatively rationalized within a simple model. Novel families of superconducting materials, particularly those based on fluoride and hydride anions, are predicted.

Keywords Ab initio calculations · Superconductivity · Oxygen · Fluorine · Hydrogen

Introduction

The fascinating variety of existing superconducting materials, in particular of those with high values of critical superconducting temperature, T_C , imposes to a chemist a *fundamental* question: what chemical elements should constitute the backbone of a successful superconductor (SC)? While some believe this question might be answered by somewhat stochastic experiments (huge “mixing matrix” screening a certain range of chemical compositions [1]), by statistical analysis [2, 3] or simply coincidentally pop out of the blue, and others think there is *no* good answer to this question, we have taken a still different approach. Given the importance of nuclear motion (including electronphonon coupling) for both low- T_C and high- T_C superconductivity [4, 5] and the existence of the *universal* scaling relationship for all temperature ranges [6] we have analyzed how certain nuclear motions influence the electronic structure of diatomic and triatomic molecular species built of one or maximum two kinds of chemical elements,

while treating metallic and nonmetallic elements on an equal basis [7–9]. Then we have linked features of vibronic coupling for the molecular and solid-state systems [10], which in turn allowed us to predict a novel family of SCs [11–13].

We now extend previous qualitative picture [7–13] to all chemical elements in the periodic table that are useful for constructing new materials [14] and supplement it with the quantitative approach, while computing for the first time the values of vibronic coupling constants in diverse systems [15]. We also predict high- T_C superconductivity in substantially covalent fluorides and hydrides.

Methods

The geometry of the molecules studied were optimized while freezing them at $D_{\infty h}$ symmetry (see [8, 9]). Such symmetric linear species serve as good models for the transition state in S_N2 reactions. Then the vibrational force constants were computed analytically [16], the most important for us being that for the antisymmetric stretching mode (this mode often showed an imaginary frequency; in such cases we formally assign a minus sign to corresponding force constant).

Calculations were performed using Becke’s three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP). We used the LANL relativistic pseudopotential followed by double zeta valence basis set for heavier elements (Br and I) and Pople’s 6-311++G** basis set for the light atoms (H, Li, F and Cl). Our calculations were performed with the Gaussian 03 package [17].

Values of force constants, k , electronic coupling elements, Δ , and vibronic coupling constants, V , were determined by fitting the Potential Energy Surfaces (PESs, scanned along the normal coordinate of the antisymmetric stretching mode, Q_{as}) to a classical three-parameter model [8]. Details of the fitting procedures are described in the Appendix.

This work is dedicated to my British friend, Peter P. Edwards, at his 55th birthday. God save dear Peter Paul.

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Results

Analysis of vibronic coupling constants in linear symmetric triatomic radicals

First, we discuss the vibronic coupling constants, V , in a series of simple triatomic radicals. Analysis of the numerical results and the relationship between V and the hardnesses of the component atoms (Table 1 and Fig. 7 in the Appendix) allows us to draw the conclusion that it is impossible to obtain large vibronic coupling constants without the presence of F or H atoms in a molecule [18, 19]. Species that do not contain these atoms (built of softer nonmetals, such as Cl, Br and I) typically have V two orders of magnitude smaller than the hardest F-based and H-based molecules (F_2H , H_2F and H_3) [20–24]. We note the interesting case of Li_3 , composed exclusively of metallic atoms—which has V and k comparable to those of I_2Cl , but the electronic coupling (Δ) in the former is much larger than in the latter. This results in the appearance of an energy minimum along Q_{as} for I_2Cl , while the potential energy surface for Li_3 is nearly quadratic with respect to Q_{as} [25].

What are the common features of the existing moderate- T_C and high- T_C superconductors?

Analysis of the existing families of SCs allows for the observation that all moderate- T_C ($23\text{ K} < T_C < 77\text{ K}$) and high- T_C ($>77\text{ K}$) superconductors must contain one of the following nonmetals: B, C, N or O. For MgB_2 [26–38] the B sublattice superconducts, while for alkali-doped fullerenes [27] it is the C cage. For more complex multinary materials, it is typically a hole-doped or electron-doped binary backbone which is predominantly responsible for superconductivity (HfN for Li_xHfNCl [28], BiO for $K_xBa_{1-x}BiO_3$ [29, 30] and CuO in all oxocuprate materials, including classical $La_{2-x}BaCuO_4$ [31] and the infinite layer model compound $(Ca_{1-x}Sr_x)_{1-y}CuO_2$ [32]). Also, other important SCs with lower T_C values exhibit a single-element or two-element backbone crucial for superconductivity, for example Si in $Na_2Ba_6Si_{46}$ [33], MoS in $PbMo_6S_8$ [34] and RuO for Sr_2RuO_4 [35] or NiC in $MgCNi_3$ [36]. Only very seldom does the superconducting scaffold contain three different elements, and most often two of them have similar valence orbital energies, so that their atomic orbitals do not give rise to distinctly separate bands in the crystal (for example $Pb_{1-x}Bi_xO$ in $BaPb_{1-x}Bi_xO_3$ [37]), or $Pd_{1-x}Ag_xH$ in $Pd_{1-x}Ag_xH_y$ [38].

In Fig 1, we plot the general qualitative relationship between the T_C values of various families of inorganic superconductors and the first ionization potential of the most electronegative element constituting the conducting backbone of each compound.

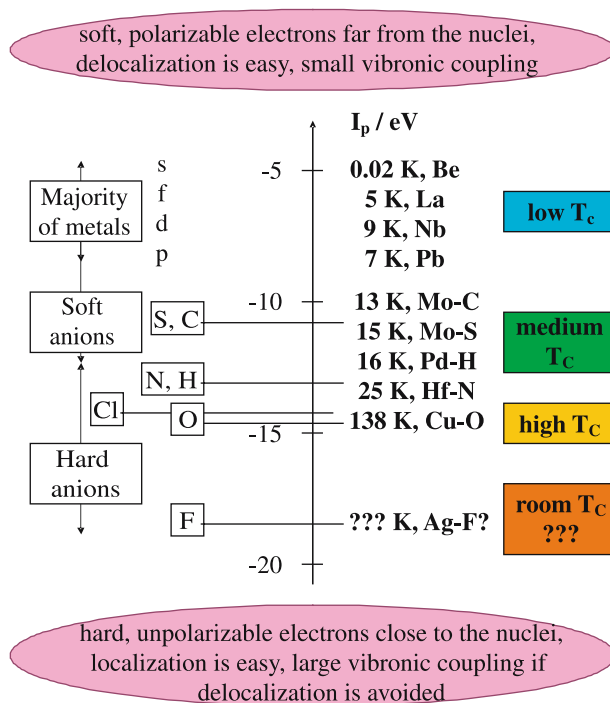


Fig. 1 Various families of inorganic superconductors with their T_C values shown versus the first ionization energy (I_p/eV) for the more electronegative of the atoms that form the conducting backbone of each compound. Note that for all superconducting salts shown here, the states at the Fermi level are composed of strongly mixed valence states of cations and anions (substantial ‘covalence’). Compare also to strong association of T_C with the work function [2]

Thus, the appearance of successful superconductivity in diverse classes of materials strongly relies on the presence of small and as hard and electronegative as possible atoms (or anions) of nonmetals [39] in the conducting scaffold of a chemical compound. This is in good agreement with our conclusions on the strength of vibronic coupling from the previous section.

Where to search for novel high- T_C materials?

The first indication from our studies is that high- T_C superconductivity cannot be found in materials built exclusively from metallic elements. The second important message is such that superconductivity with T_C values higher than those for oxides should be found in hydride and fluoride materials [40, 41]. The third qualitative extrapolation (see Appendix) is that providing metallic conductivity using “hard”, unpolarizable valence electrons at extremely low-lying Fermi level, is technically difficult (due to the preference for electron localization) but it may ultimately deliver room temperature SC. For this purpose, however, charge localization, inherent for systems built of strongly electronegative atoms, should be avoided by (i) bringing

into the conducting backbone other electronegative species, which will compete for valence electrons with atoms of nonmetals [42], (ii) introducing doping and (iii) using adequate crystal engineering and providing the desired electronic dimensionality.

The “materials aspect” of vibronic coupling is illustrated in Fig 2. We emphasize elements that provide moderate- T_C and high- T_C superconductivity in existing materials (in green), those we predict should deliver high T_C values due to large vibronic coupling constants (in blue), and those, for which T_C enhancement is expected predominantly due to their small atomic mass (in bright blue).

In the spirit of our earlier observations that the crossing of electronic potential energy surfaces enormously increases vibronic coupling strength [9, 10], we now need to search for the appropriate elemental partners for the promising fluoride and hydride anions, which could then the form binary scaffold of novel prospective SC materials.

Thus, for fluorine, combinations with Ag [11–13] and Hg at high-oxidation states [43], and with Sb, Bi or Tl [44], show remarkably large covalence [42] and merit further studies. For hydrogen, H-rich molecular hydrides of Si [45], B, P, W [46], Ta [46] and Re [47], as yet unknown multinary hydrides of Eu [48], Yb [48, 49] and Tm [49] and novel multinary hydrides of noble metals (Pd, Ag and Pt) are of interest. Along with large electron–phonon coupling, hydrides should also benefit from very large phonon frequencies.

Fig. 2 Elements of the Periodic Table that provide moderate- T_C and high- T_C superconductivity in existing materials (in green), those we predict should deliver high T_C values due to large vibronic coupling constants (in blue), and those, for which T_C enhancement is expected predominantly due to small atomic mass (in bright blue). Elements useful for the construction of new materials are in dark yellow, the remaining ones in bright yellow. Note, H is placed here in Group 17, by He, as H needs one e^- to achieve the configuration of a doublet

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I																	1	2
II	3	4											5	6	7	8	9	10
	Li	Be											B	C	N	O	F	Ne
III	11	12											13	14	15	16	17	18
	Na	Mg											Al	Si	P	S	Cl	Ar
IV	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
V	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
VI	55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
VII	87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
			57	58	59	60	61	62	63	64	65	66	67	68	69	70		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
			89	90	91	92	93	94	95	96	97	98	99	100	101	102		
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Nb		

The analysis presented here gives, of course, no detailed recipe for the stoichiometry of novel SC materials, and does not guarantee the appearance of SC at any particular composition. This is obvious given the enormous sensitivity of known SCs to the type and level of doping [50], to minor distortions of the crystal structure [51], etc. However, given myriads of multinary chemical compounds which can be obtained from all chemical elements [14], our approach benefits from a significant reduction of potentially interesting combinations of elements, and allows us to concentrate on specific, narrow families of chemical compounds [52].

Appendix

Determination of vibronic coupling constants in linear symmetric triatomic radicals

Fig. 3 shows the Potential Energy Surface (PES) along the antisymmetric stretching coordinate, Q_{as} , of the symmetric (at $Q_{as} = 0 \text{ \AA}$) linear triatomic radical, here represented by Br_2H

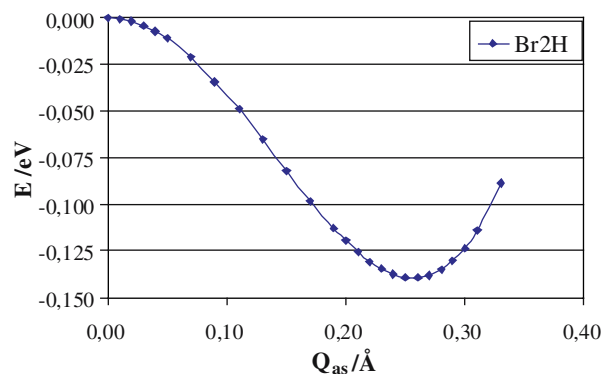


Fig. 3 The computed PES along the antisymmetric stretching coordinate, Q_{as} , of the symmetric linear radical, Br_2H

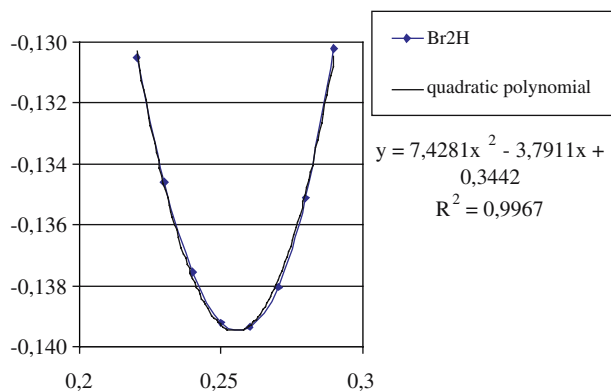


Fig. 4 The computed PES of Br_2H in the vicinity of energy minimum. Force constant at a minimum, $k'' = 14,856 \text{ eV } \text{\AA}^{-2}$, can be calculated from the quadratic fit

From this plot, two separate force constants have been calculated: one corresponding to the imaginary antisymmetric stretching mode at $Q_{\text{as}} = 0 \text{ \AA}$, further called k'_- , and force constant at the minimum of the PES (here at $Q_{\text{as}} = Q_{\text{min}} = 0.26 \text{ \AA}$), further called k'' . The notation used here is identical as that used in Ref. [8]. Typically, we have used between 4 and 10 points on the PES for the quadratic fit (see Figs. 4, 5 and

Using the known values of k'_- and k'' , the value of the force constant in the hypothetical absence of vibronic coupling, k , has been determined from the best fit to the equation: $k'' = k - k^3/(k - k'')^2$. In case of Br_2H , the value of $k = 66.1 \text{ eV } \text{\AA}^{-2}$ was obtained.

The preliminary estimates of the values of the vibronic coupling constant, V , and of the electronic coupling constant, Δ , was calculated as follows. First, $(V^2/\Delta) = k - k_- = 75.08 \text{ eV } \text{\AA}^{-2}$. Second, $V = \{[(k'')^2 - (V^2/\Delta)^{-2}]/(Q_{\text{min}}^2)\}^{-0.5}$. Thus, $V = 36.3 \text{ eV } \text{\AA}^{-1}$ and $\Delta = 17.5 \text{ eV}$. These preliminary estimates were used as starting values in the fit of the computed PES to the equation $E = 1/2kQ_{\text{as}}^2 + (\Delta^2 + V^2 Q_{\text{as}}^2)^{0.5} + \Delta$. From the fit, new set of parameters has been obtained: $k = 75.5 \text{ eV } \text{\AA}^{-2}$, $\Delta = 22.0 \text{ eV}$, and $V = 43.1 \text{ eV } \text{\AA}^{-12}$.

The final values of k , V and Δ for other chemical species have been determined in an analogous way.

¹The value of the energy at $Q_{\text{as}} = 0$ has been normalized to zero for all systems. This is why Δ needs to be added to the equation for the energy in comparison with Eq. 1 in Ref. [8].

²In the three-parameter model one deals with two electronic states coupled through one normal vibration. This means that values of k , Δ and V determined here for real molecules do not refer to any excited state but rather represent the global effect of coupling of the ground state with all excited states of appropriate symmetry. For example, the ground state of the H_3 radical transition state (Σ_u^+) couples with *all* excited Σ_g^+ states via a normal vibration of σ_u symmetry (i.e. along Q_{as}). Overall coupling is so strong in this case that distortion leads to an energy decrease of the ground state.

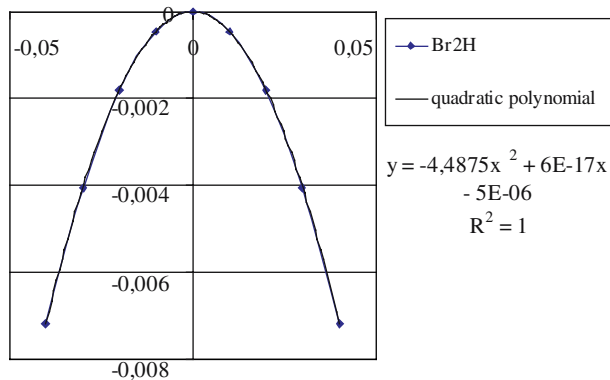


Fig. 5 The computed PES of Br_2H in the vicinity of energy maximum (at $Q_{\text{as}} = 0 \text{ \AA}$). Force constant at a maximum, $k'_- = -8,975 \text{ eV } \text{\AA}^{-2}$, can be calculated from the quadratic fit

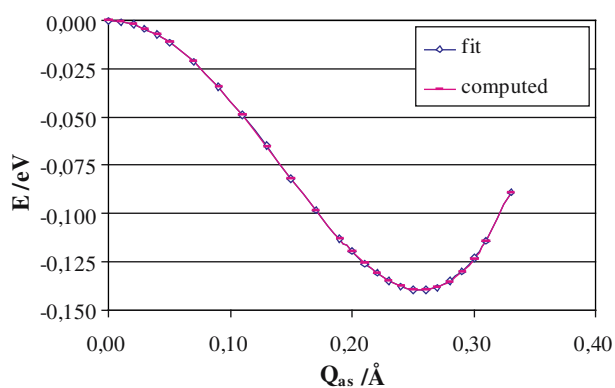


Fig. 6 Comparison of the computed and fitted PES of Br_2H

Figure 6 shows the comparison of computed and fitted PES for Br_2H . The fitted PES reproduces all essential features of computed PES, including the position of Q_{min} . The fitted and computed curves are virtually undistinguishable.

In Table 1, we show the value of the optimized E–X bond length, R_0 , for a variety of molecules, the analytical value of the force constant for the antisymmetric stretching, k_{anal} , position of the minimum (along Q_{as}) of PES, ΔQ_{as} , value of force constant in the absence of vibronic coupling, k , electronic coupling element, Δ , and the vibronic coupling constant, V , determined from the fitting procedure using a three-parameter model [8].

For F_2H , H_3 but also for Li_3 (and for other species that do not exhibit an imaginary frequency along Q_{as}), the three parameters of the fitting procedure are strongly correlated with one another, i.e. equally good fits may be obtained for various sets of these parameters. This implies large relative errors in determining k , Δ , and V . We have omitted the fitting procedure for such molecules, while making an exception for Li_3 , in order to compare it to interhalogen compounds.

Table 1 Values of R_0 , ΔQ_{as} , k , Δ , and V , and errors of k , Δ and V (for details see text)

E_2X	R_0 (Å)	k_{anal} (mDyne Å ⁻¹)	ΔQ_{as} (Å)	k (eV Å ⁻²)	Δ (eV)	V (eV Å ⁻¹)
F ₂ H	1.1164	-2.84	0.17	363 ± 71	120 ± 48	214 ± 63
H ₂ F	1.1500	-3.37	0.25	314 ± 4.4	91.2 ± 2.6	178.4 ± 3.6
H ₃	0.9310	-0.32	0.07	250 ± 57.6	121.7 ± 57	175 ± 61
Cl ₂ H	1.5000	-0.67	0.15	162 ± 22.2	64.9 ± 18.1	103.9 ± 21.4
H ₂ Cl	1.5000	-0.89	0.20	123 ± 3	31.5 ± 1.5	64.8 ± 2.3
Cl ₂ F	1.9470	-3.71	0.29	92.0 ± 3.2	23.9 ± 1.8	50.8 ± 2.6
H ₂ Br	1.6640	-0.74	0.22	88.5 ± 1.3	22.7 ± 0.7	47.0 ± 1.0
Br ₂ H	1.7112	-1.48	0.26	75.5 ± 1.7	22.0 ± 1.0	43.1 ± 1.4
I ₂ H	1.9057	-1.30	0.28	62.7 ± 5.3	20.4 ± 3.7	37.9 ± 4.9
H ₂ I	1.8090	-0.29	0.15	69.1 ± 0.5	16.6 ± 0.3	34.8 ± 0.4
Br ₂ F	2.0890	-1.35	0.23	68.3 ± 29.6	12.3 ± 10.7	31.1 ± 19.5
F ₃	1.6322	-32.5 ^a	0.25	52.5 ± 2.3	1.61 ± 0.20	14.1 ± 0.82
I ₂ F	2.2110	-0.66	0.18	21.4 ± 1.8	0.33 ± 0.14	4.57 ± 0.63
Cl ₃	2.2590	-0.96	0.15	16.4 ± 1.6	0.76 ± 0.17	3.96 ± 0.59
Br ₂ Cl	2.4870	+2.01 ^a	0.17	10.2 ± 0.3	0.25 ± 0.02	2.16 ± 0.09
I ₂ Cl	2.6777	-2.48	0.24	8.2 ± 0.5	0.27 ± 0.03	2.15 ± 0.15
I ₂ Br	2.8800	-6.17	0.11	7.1 ± 0.25	0.08 ± 0.01	0.99 ± 0.05
Br ₃ ^{b,c1}	2.6710	-0.21 ^a	NA			
I ₃ ^{c1}	3.0334	+0.44 ^a	NA			
F ₂ Cl	1.7730	+4.32	NA			
F ₂ Br	1.9448	+3.20	NA			
F ₂ I	2.0497	+3.04	NA			
Cl ₂ Br	2.4450	+0.25	NA			
Cl ₂ I	2.5744	+1.19	NA			
Br ₂ I	2.8191	+1.01	NA			
Li ₃	2.8850	+0.365	NA	3.5 ± 0.6	1.1 ± 0.7	1.4 ± 0.7

Typical error of the ΔQ_{as} value is ± 0.005 Å

^a Erroneous analytical values of force constants at $Q_{as} = 0$ are computed for these molecules. Note that k_{anal} corresponds to k'_- from the model, and not to the fitted k !

^b Problems with reliable determination of PES; perhaps more than one low-lying electronic states is involved in vibronic coupling with the ground state

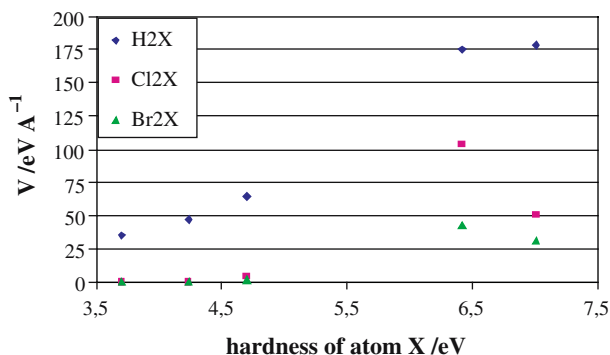


Fig. 7 Values of vibronic coupling constant, V , versus Pearson's hardness, η , of bridging element X, for three families of molecules (H_2X , Cl_2X and Br_2X). Values of V for I_2X molecules have not been shown as they are nearly the same as those for corresponding Br_2X ones. Values of V for molecules, which are not unstable along Q_{as} are very small, and have been taken as null

Vibronic coupling constants versus Pearson's hardness of the bridging atom

In Fig. 7 we show values of V plotted versus Pearson's hardness, η , of the bridging element X (η /eV: 7.01 F, 6.42 H, 4.70 Cl, 4.24 Br, 3.70 I).

The harder the bridging atom ($F > H > Cl > Br > I$), the larger the value of V . For the same bridging atom, the harder the end atoms ($H > Cl > Br$), the larger the value of V ³. Confirmation of a possible decrease of V

for very large values of hardness, requires a more representative statistical probe.

The T_C values for selected families of materials versus the Mulliken electronegativity of the most electronegative element

In Fig. 8, we show experimental values of T_C multiplied by the $m^{1/2}$ factor (i.e. T_C divided by the factor that is proportional to the pre-exponential expression from the BCS theory), plotted versus Mulliken electronegativity, μ , of the most electronegative atom in the compound considered. Numerical data is collected in Table 2

The expected values of $(T_C m^{0.5})$ for N, H, P, C, Cl and F-based materials can be translated back to the expected values of T_C in these materials. The fit indicates the possibility of great improvement of the T_C values for phosphides (61 K), carbides (102 K), and nitrides (136 K), while it delivers astonishingly high T_C values for fluorides (268 K = -5°C) and hydrides (> 490 K, > 210 C).

³Values of V are very large for interhalogen and H-containing compounds. This is why enormously large pressures are required to metallize halogens, while no metallization of H_2 has been achieved so far using static pressures.

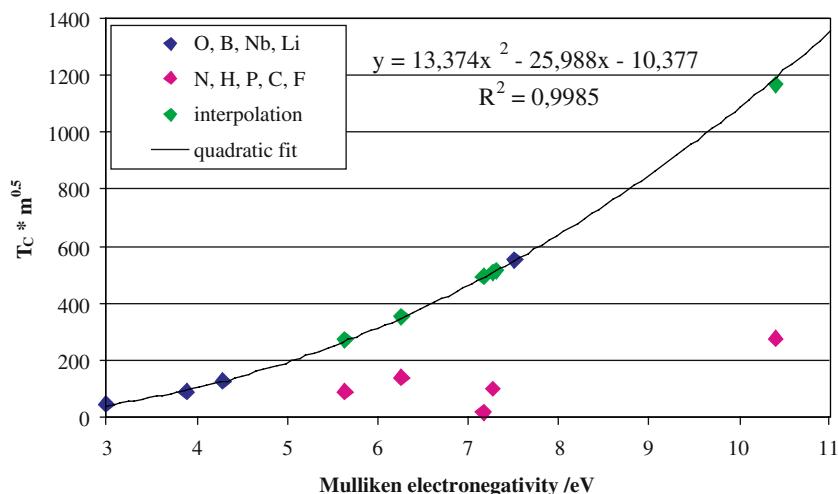


Fig. 8 Value of the $(T_C m^{0.5})$ product (T_C in K, m in atomic mass units) versus the Mulliken electronegativity, μ , of the most electronegative element from the given compound. Quadratic fit (solid line) is shown for the data for record—holding oxocuprate, MgB_2 , classical Nb and Li under high pressure (dark blue points). Experimental points for best-known nitride, hydride, phosphide carbide and fluoride materials are shown in pink. We think these values may be improved a lot. Green points correspond to the maximum expected values of the $(T_C m^{0.5})$ product for N, H, P, C, Cl and F-based materials, and were calculated using fitted function of μ . For details see Table 2

Table 2 Values of the Mulliken electronegativity of the most electronegative element, μ , critical superconducting temperature, T_C , square root of the atomic mass of the element considered, $m^{0.5}$, and of the $(T_C m^{0.5})$ product, for several representative families of superconductors

Compound	Family	μ (eV)	T_C (K)	$m^{0.5}$	$T_C m^{0.5}$
$Hg_2Ba_2Ca_3Cu_4O_x$	O	7.53	138	4.0	552
MgB_2	B	4.29	38.5	3.3	128
Nb	Nb	3.88	9	9.6	89
Li @ 80 GPa	Li	3	16	2.6	42
Li_xHfNCl	N	7.27	25.5 (136)	3.7	99 (508)
$(Pd_{1-x}Ag_x)H_y$	H	7.17	16 (491)	1.0	16 (491)
MoRuP	P	5.24	15.5 (61)	5.6	86 (345)
Cs_3C_{60} @ 14 GPa	C	6.27	40 (102)	3.5	139 (352)
**a **b $BeAgF_4$	F	10.41	64 (268)	4.4	279 (1168)
	Cl	7.31	(86)	6.0	(514)

^aSee Ref. [39]

^bSuperconductors containing halide anions are, of course, known, to mention Li_xHfNCl , $Sr_2CuO_2Cl_2$, and carbide chlorides of rear earth metals ($RECl_2$) as examples. However, Cl plays a secondary role for these compounds, and often may be substituted by another halide. To the best of our knowledge, superconductivity relying on electron transfer genuinely involving the Cl(p) orbitals has not been observed so far. Maximum values of the T_C and $(T_C m^{0.5})$ for nitrides, hydrides, phosphides, carbides, fluorides and chlorides, predicted from interpolation of the $(T_C m^{0.5})$ values for known superconductors, are given in parentheses. See also Fig. 8

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- We know now 116 elements (1–116), while 88 of the most stable ones may be used by a chemist for synthesis of novel materials (1–42, 44–60, 62–83, 89–94) (the usefulness of He, Ne and Ar is, of course, very limited). The number of binary combinations of these 88 elements is equal to 7656, the number of ternary ones more than 658 thousand, and for quaternary ones nearly 56 million (given that one stoichiometric ratio is chosen and fixed!). Systematic synthesis of so large number of compounds exceeds human possibilities in terms of the required time and funding
- Selected results related to this work have been presented by the author during the Modelling and Design of Molecular Materials workshop, Wrocaw (Poland) 17 September 2004. Superconductivity has been then discussed in a broad framework including metallization of nonmetals and semiconductors, influence of the external pressure on the Peierls distortion, dynamics of nuclear motion of the localized/delocalized mixed-valence species (molecular and in the extended phases), and enhancement of vibronic coupling in the vicinity of the avoided crossing of potential energy surfaces
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18. As we have noted in previous work, the vibronic stability of A_2B molecules, where A is the more electronegative element, is much larger than that of B_2A molecules. Thus, species like F_2Cl , F_2Br , and F_2I , and also Cl_2Br , Cl_2I and Br_2I , are inevitably stable along Q_{as} , despite the fact that they contain strongly electronegative elements. This is inherently connected with the preference for negatively charged atoms at the ends, and for the positively charged atom in a bridging position, even for homonuclear molecules.
 19. It is important to note that V is large both in these H-containing molecules, where H serves formally as a cation (as in H_2F), and in those where H serves formally as an anion (as in I_2H). This shows that vibronic coupling connected with the electron transfer between H^+ and H^0 , and also between H^- and H^0 , is very strong
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 39. Compare values of hardness: $\eta(F) = 7.01$ eV, $\eta(H) = 6.42$ eV, $\eta(O) = 6.08$ eV, $\eta(Cl) = 4.70$ eV. See also Ref. [11–13] and Grochala W, Porch A, Edwards PP (2004) *Solid State Commun* 130:137–142
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 52. “Ours is a material(s) world, but remarkably, we are still unable to predict the chemical composition, the crystal structure and the physical properties of the most known, and all emerging new materials.” Citation from Edwards PP and coauthors, “*The fundamental properties of materials*”, application to The Leverhulme Trust