The Matthias Rules: Origins and Influence

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Abstract

Developed by Bernd Matthias, the "Matthias Rules"(MR) offer empirical guidelines that help determine the necessary conditions for the occurrence of superconductivity in elements, compounds, and alloys. Through the analysis of numerous experimental results detailing the discovery of new superconducting compounds, Matthias generalized which parameters are conducive to givising rise to higher superconductive transitions in materials. By simply considering the properties of individual atoms, he empirically deduced a functional form of T_c which depends on the number of valence electrons per atom. Furthermore, he asserted that crystal structure, atomic volume, and atomic mass also play significant roles in inducing superconductive transitions. This helped lead to the understanding that different types of "unconventional" superconductors exist which exhibit mechanisms for superconductivity beyond the electron-phonon interactions described by BCS theory. The origins and impacts of these assertions provided by Matthias are duly discussed. Deviations from these empirical rules are also presented and considered.

Background

Since the discovery of superconductivity in Hg by Kammerlingh Onnes in 1911 and soon after Pb and Sn in [1,2], the undertaking of finding higher T_c superconductive materials has proven to be a provocative challenge riddled with complexity. With the ultimate hope of someday raising the superconducting transition of a material to room temperature, physicists had been attempting tried to provide a theoretical solution to model this transition. In so doing, a common approach was to study elements, such as gold, that were known to have low resistivity values at room temperature. It was not until the work of Walther Meissner and his collaborators in 1930 that certain compounds of metals comprised of nonmetallic elements such as nitrogen, carbon, and sulfur were discovered to also exhibit superconducting characteristics at solid hydrogen or liquid helium temperatures [3,4].

Motivated both by the work on discovering superconducting pure metals, as well as Meissner's work on interstitial compounds, Bernd Matthias, along with John Hulm began searching for superconductivity in various elements, alloys and compounds alike, including various borides, nitrides and silicides [5,6]. As opposed to Meissner's method of measuring the disappearance of electrical resistivity to discover superconducting transitions, Matthias and Hulm (rather ironically) searched for transitions in superconductivity by utilizing the fact that superconductors expel applied magnetic fields [7], an effect which came to be known as the Meissner effect. They measured this change in magnetic induction via a magnetic permeability apparatus, equipped with cryostat for cooling down a sample to

liquid helium temperatures, as well as a high sensitivity galvanometer [8]. A small external magnetic field was applied to a cooled sample, and the initial permeability of said sample was attained. Depending on the direction of current flow measured by the galvanometer, it could be determined whether the sample exhibited signs of superconductivity or ferromagnetism [9]. This proved to be advantageous over transport measurements, as superconducting filament formation could skew readings, and lead to misinterpretation of a bulk superconducting state. Essentially, small filaments would act as superconducting pathways for charge carriers, when the bulk of the material actually had a non-zero resistance [10]. By measuring magnetic susceptibility, Matthias and Hulm were able to seemingly overcome these anomalous effects and gain a more accurate understanding of which phases were responsible for superconducting transitions in multiphase samples.

With these tools in hand, Matthias took to finding higher T_c's in a variety of materials, using the periodic table as a guide. Focusing on two distinct sections of the table, from groups 3A to 8A and groups 2B to 4B respectively [8], Matthias employed a quantitatively methodical approach to discover as many new superconductors as possible, with the hopes of gaining insights as to what spurs higher superconducting transitions temperatures [11]. From this, he arrived at certain conclusions about the magnetic and electronic nature of elements that form superconductors, not only for pure elemental systems but also for compounds, as exhibited in his work on the cobalt-silicon system [6,12]. Although $CoSi_2$ was not initially expected to demonstrate superconductive behavior, as cobalt is ferromagnetic and silicon is a semiconductor, the coalescence of the two proved to be superconducting, indicating that much was unknown about the underlying mechanisms behind superconducting behavior, especially in compounds and alloys.

Perhaps the most successful finding from this foray came with Matthias's collaborators at Bell Laboratories, notably Theodore Geballe (with whom Matthias shares the 1970 Buckley Prize) on their work on Nb_3Sn [13]. The group determined the compound to exhibit a superconducting transition temperature of 18 K, the highest known at the time[13]. Not only did this discovery corroborate some of Matthias's earlier generalizations, but it also provided insights on the impact crystal structure had on superconducting transitions. As it was found that Nb_3Sn exhibits a β-Wolfram structure, similar to V_3Si, the material with the previously known highest T_c, it became apparent that lattice spacing and structure could also heavily impact superconductive behavior in compounds [14].

After observing the superconducting behavior of a multitude of elements and interpolating correlations that seemingly described patterns relating to crystal structure and grouping in the periodic table, Matthias subsequently formulated an empirical curve to fit T_c data attained primarily from Rhodium, Tungsten, and Molybdenum compounds [15]. This empirical fit was accordant with the numerous adages previously made by Matthias, and had parameters of atomic volume, atomic mass, and number of electrons per atom, though electron concentration remained most influential [16]. An elaboration of this empirical formula, along with other guidelines derived from Matthias' previous observations on the nature of superconducting transitions came to be known as the "Matthias Rules".

Matthias Rules

In 1957, Matthias published a chapter in the second volume of *Progress in Low Temperature Physics* called "Superconductivity in the Periodic System", in which he outlines his generalizations [8,11,15,16] along with other observed behaviors for both purely elemental and compound/alloy systems [17]. These "rules" are outlined and elaborated on as follows:

1. Elemental Systems

1. Superconductivity does not appear in elements where, for n being the number of valence electrons per atom, n is fewer than 2 or greater than 8 [11,15]. Therefore, for an element to be superconducting[1,2]:

$$2 \leq n \leq 8$$

2. Only specific metals seem to exhibit superconductivity[3]. Thus, superconductivity is generally not found in:
    a. Ferromagnetic or antiferromagnetic elements
    b. Nonmetals, semiconductors, or semimetals

3. A purely qualitative empirical function T(n) can model superconducting transition temperature as a function of valence electrons per atom. A plot of such a periodic function T(n) for transition metals can be seen in figure 1. For transition metals, peaks occur for odd values of n, and minima occur for even values. For non-transition metals, T(n) increases monotonically with n.

4. It is observed that:

$$T_c \propto \frac{V^x}{\sqrt{M}} \qquad 4 < \mathrm{x} < 5 \qquad [1]$$

    where V and M are the atomic volume and atomic mass, respectively.

5. Crystal structure is also observed to play a seemingly influential role in the presence of superconducting behavior. Of the numerous superconducting elements, crystal and hexagonal symmetries proved most favorable in giving rise to superconductive

[1] This claim was made for observable temperatures down to 1K [11].

[2] In later works [18], this was statement was extended to situations where "n is appreciably greater than 1 or less than 10", when considering temperatures below 1K

[3] These claims are made by referencing a compiled list of known superconducting elements at the time, and organizing them by periodic structure [17,19]

transitions. These variations can attribute 20-30% change in Tc. The aforementioned rules reduce to the singular statement:

$$T_c \sim c\frac{V^x}{\sqrt{M}}T(n), \qquad [2]$$

$$where\ 4 < x < 5\ , \quad 2 \leq n \leq 8$$

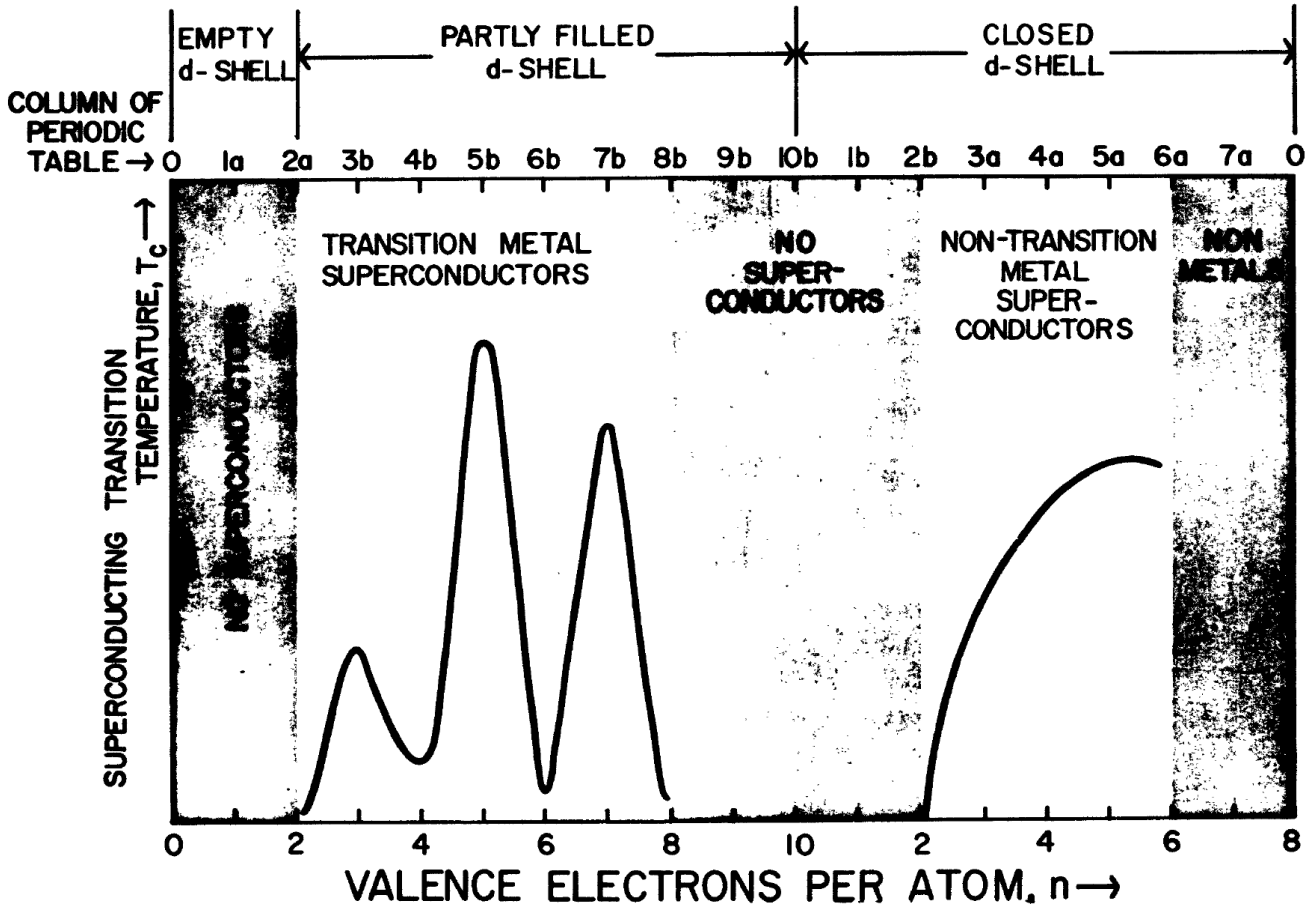

Figure 1: Empirical formulation of critical transition temperature behavior ranging through the periodic system, T(n)[17].

2. Compounds and Alloys

Due to larger variation in crystal structure and lattice parameter that is inherent in superconducting compounds, slight modifications can be made to the mentioned for elemental systems above to apply to compounds and alloys. These modifications are rooted within the chapter originally written by Matthias, and further expanded on by ensuing works. The modified Mathias Rules for compounds and alloys are as follows:

1. For n now denoting the number of valence electrons per atom in the alloy or compound, it again follows that for a material to posses superconductive behavior:

$$2 \leq n \leq 8 \quad [3]$$

2. Materials with the electronic properties of nonmetals, semimetals, and semiconductors do not exhibit superconducting behavior. Antiferromagnetic materials do not exhibit superconductivity, though some materials which exhibit ferromagnetism resulting from f-orbital spins (as opposed to partly filled d-subshells) can be superconducting in nature [20,21].

3. As with pure elements, a similar empirical formula can describe T(n) which follows the same qualitative behavior apparent in figure 1, though the peaks are shifted[4].

4. As opposed to purely elemental systems, the critical transition is said to behave as:

$$T_c \propto V^x \quad [4]$$

$$where\ 5 < x < 10$$

Though the vale of x varies, "seven is the dominant one"[17]. Though T_c also has some dependence on the different atomic masses per element in a compound or alloy, it is said that some effective volume dependence could be apparent, with a value between that of the reduced mass and the geometric mean of the components. Furthermore, simple average mass values did not yield agreement with the elemental rules.

5. Cubic and hexagonal symmetries, as well as the β-Wolfram structure, are favorable for superconducting transitions compounds and alloys. As opposed to purely elemental systems, whose T_c's can often times rise due to strains or imperfections, it was observed that imperfections in these more complex systems leads to a lowering of T_c.

Theory

In Matthias' words, "Most theories of superconductivity, in my opinion, are merely descriptions. They become theories only when they are able to predict" [22]. As such, he remained exceedingly critical of the dominant theories of superconductivity at the time, and maintained a highly empirical approach to his research.

The dominating theoretical analogue to the Matthias Rules at the time was Bardeen-Cooper-Schreiffer (BCS) theory [23], which gives a relation for the critical transition temperature as:

[4] As these peaks are describing empirical averages, the shifts vary independently for each material.

$$kT_c \sim \hbar\omega \exp\left[-\frac{1}{N(0)V}\right] \quad [5]$$

where k is the Boltzmann constant, $\hbar\omega$ is the average phonon energy, N(0) is the number of electrons per unit energy near the Fermi surface, divided by the volume of the sample, and –V denotes an average net interaction energy of electrons near the Fermi surface per sample volume. Using this fact, David Pines addresses the case of the non-transition metals by modeling the system as a free electron gas, neglecting the effect due to a periodic lattice [24]. In such a system, the Coulomb interaction between two electrons experiences a "screening", which is given as a function of the inverse Fermi-Thomas screening length, k_s, defined as:

$$\frac{k_s}{k_0} = .814 r_s^{1/2} \quad [6]$$

where k is wave-vector and r is a new quantity representing electron spacing. The electron spacing is defined as:

$$r_s a_0 = \left(\frac{3}{4\pi N_e}\right)^{1/3} \quad [7]$$

where a_0 is Bohr radius and N_e is electron density. Using these definitions, Pines derives a complicated expression for electron interaction, -V, with phonon term that is attractive in nature, and a Coulomb term that is repulsive, written as:

$$-N(0)V = a^2\left\{\left[1 - (4Z^*)^{\frac{2}{3}}a^2\right]\ln\left(\frac{1+a^2}{a^2}\right) + (4Z^*)^{\frac{2}{3}}a^2 \ln -^1\left(\frac{+(4Z^*)^{\frac{2}{3}}a^2}{(4Z^*)^{\frac{2}{3}}a^2}\right) + \frac{(4Z^*)^{\frac{2}{3}}a^2}{1+a^2} - 1\right\} \quad [8]$$

where Z* is effective ion valency (similar to n) and a is defined as $a^2=r_s/6.02$. Pines argued that the criterion for superconductivity is that V be negative, meaning the phonon-induced attractive interaction must dominate over short-range Coulomb repulsion. This shows agreement with the Matthias Rules, as increasing the screening parameter k_s reduces the phonon term less than the Coulombic term. As can be seen from combining equations 4 and 5, k_s increases with atomic volume. Thus, this suggests that larger atomic volumes are better for superconductivity, which is accordant with equation 1.

Pines' work, however, only applies to non-transition metals, but fails to account for other mechanisms apparent with increasing n. As such, the empirical formulation of figure 1 indicates some disagreement with BCS theory. As maxima can clearly be seen for n=3, 5, and 7, and minima for n=2, 4, and 6, this would suggest a possible spin-exchange-related mechanism [18] beyond the electron-phonon interaction described by BCS theory. Experiments where the transition temperatures of Ti and Zr were raised by the addition of magnetic impurities also suggest this [25]. This, however, does agree with the Ginzburg-

Landau phenomenological model, where 2 "types" of superconductors are described suggesting interactions beyond that of BCS [26].

Thus, BCS theory fails to describe interactions beyond the electron-phonon interactions mediated by the formation of cooper pairs. Furthermore, BCS fails to provide an explanation as to exactly which criteria are responsible for inducing high T_c's, or even inducing transitions at all for elements, alloys and simple compounds [27]. Though this is, Matthias's experimental results helped lead to the development of new theoretical models describing the mechanisms of superconductivity. One such mechanism could be described by the "hole" theory of superconductivity, which proposes that superconductivity results from Coulomb interactions, as opposed to electron-phonon interactions, from hole carriers, which conduct through a network of closely-spaced negatively charged anions"[28].

Deviations From Matthias Rules

Even before the rules had been established, Matthias himself noted some exceptional cases. An example of this would include the borderline cases of Cd and Zn for which n=2 [11]. As they both exhibit c/a ratios of 1.84, which is considerably different than the necessary c/a=1.633 required for hexagonal closed-pack structure [15], a superconducting transition is able to occur. On the other hand, elements such as Magnesium with n=2 do not exhibit superconducting behavior. Thus, other complexities can possibly dominate the interaction at the limit of n being 2 or 8.

Additionally, with the introduction of high-temperature (HT_c) superconducting ceramics, including YBCO [29], Matthias' generalizations further failed. As these HT_c materials had a lower symmetry apparent with a layered structure, as opposed to Matthias's observation that higher symmetry systems are more conducive towards superconductivity, it became clear that systems existed beyond those predicted by the Matthias Rules which exhibit superconducting behavior. Finally, iron-based superconductors are antiferromagnetic at low doping (or pressure) [30].

At the Second Rochester Conference on Superconductivity in d- and f-Band Metals in 1976, Matthias gave a talk called "Some Surprises in Superconductivity", in which he said "Once upon a time, the electron per atom ratio (e/a) as a criterion for transition temperatures, worked beautifully. Well, it doesn't work so well any longer", in reference to the failure for newly discovered molybdenum sulfides and selenides to agree to the Matthias Rules [31]. Though these materials have an e/a ~6, a condition which would suggest a low transition temperature by the Matthias Rules, they display a relatively high T_c. As a result, Matthias asserted that this could partly be due to the intrinsic immiscibility of such compounds. Thus, he postulates a new criterion for superconductivity in this system by stating "only those elements which will not react at all with molybdenum alone form superconducting compounds with Mo_3S_4 and Mo_3Se_4, S or Se". Thus, the failure for certain elements to react (in this case with Mo), introduces an instability at the microscopic level, which in Matthias's opinion was "at present one of the answers for the superconductivity of these compounds"[31].

Conclusion

The Matthias Rules provide a set of guiding principles to help discover new superconducting materials. An empirical formulation of these guidelines is dependent on atomic volume, atomic mass, the number of electrons per atom, and crystal structure. Variations of these rules apply to both purely elemental systems as well as some compounds/alloys. These experimentally based generalizations suggest interactions responsible for the occurrence of superconductivity beyond the phonon-mediated method described by BCS. Though new developments in the field of high-temperature superconductivity have rendered some of these generalizations outdated, Bernd Matthias and his formulation of the Matthias Rules helped facilitate the discovery of hundreds, if not thousands of new superconducting materials. In so doing, Matthias illustrated that an experimental approach to solving the superconductivity puzzle provides valuable clues that offer insights beyond those postulated by theory (at least for now), which can be critical to constraining the myriad of theories formulated each year to describe HTc in the modern day. With this spirit of inquisitiveness, and more advanced empirical and theoretical models, it is only a matter of time until new patterns in T_c emerge, which can ultimately lead closer to the development of room-temperature superconductivity.

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