# The search for high-temperature superconductors

Although superconductivity at room temperature will always remain a pipedream, temperatures as high as 25–30 K are a realistic possibility and will trigger a technological revolution.

Bernd T. Matthias

Since 1911 superconductivity at room temperature has been the dream of scientists and science-fiction writers alike. Unfortunately for superconductivity, the boundary between these two dream worlds has become totally blurred during the last decade. Still, today, superconductivity at room temperature together with controlled thermonuclear fusion are often mentioned as the two most important and crucial problems in physics relevant to the needs of society. Controlled fusion has now become a distinct possibility, and its progress over the last twenty years has covered many orders of magnitude. During this same time, superconducting transition temperatures have expanded from a range of 0.4 K to 16 K to a range stretching from 0.0002 K to 21 K.[1,2] If this upper limit could be further increased, not by another order of magnitude, but by a factor of as little as 1.2, or as large as 1.5, superconductivity, while still far from room temperature, would revolutionize our technology. This revolution would encompass electric power transmission, electric motors, high-field electromagnets, and the metallurgy of magnetic suspensions as a whole. In this article I will explain why I believe that this factor of 1.5 is a distinct possibility. I will also explain why room-temperature superconductivity (regardless of a thousand statements by theorists and an equal number of theories) is—in my opinion—pure science fiction.

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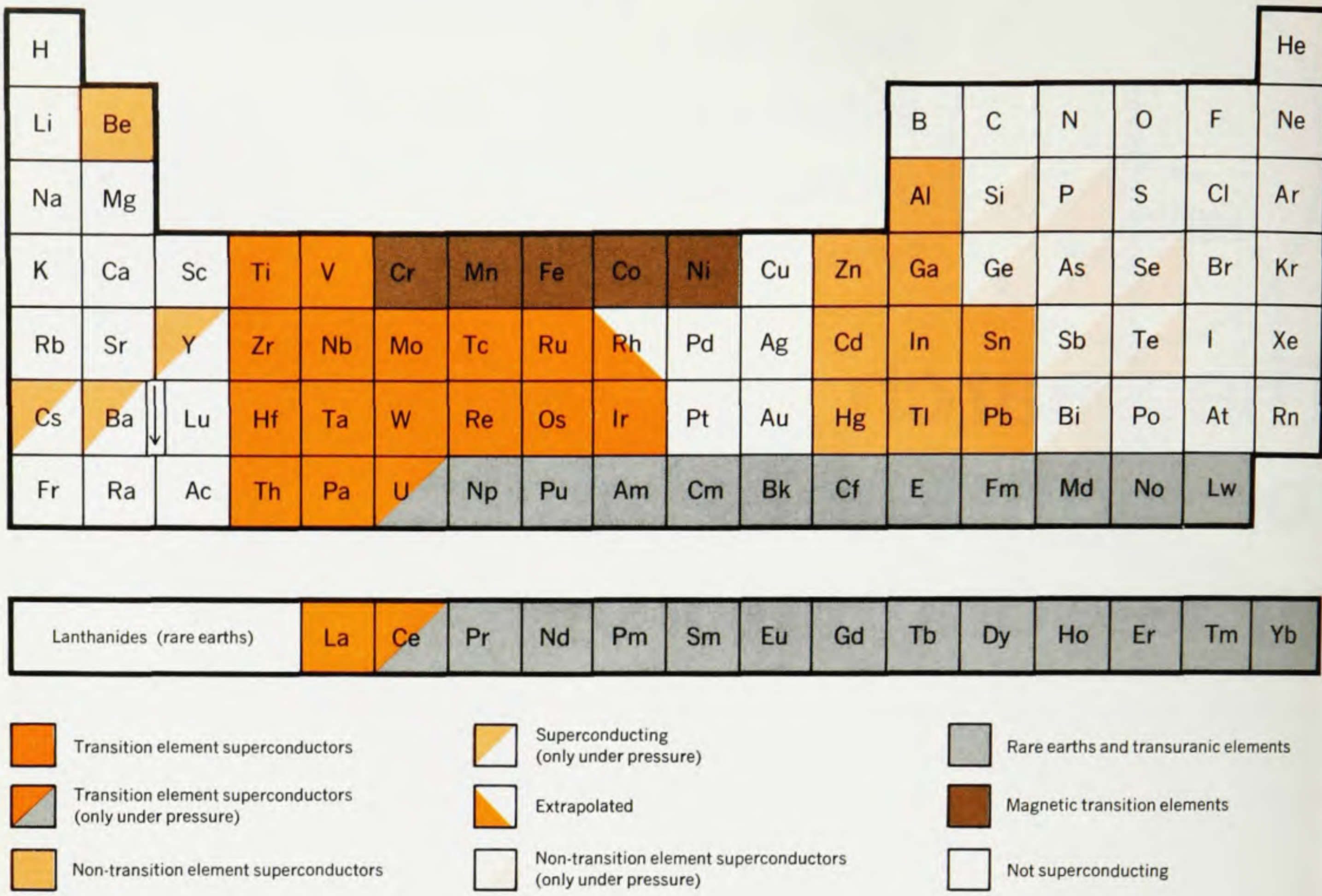
During the past twenty years a great many superconductors, both elements and compounds, have been discovered. They are all accounted for and classified in Ben Roberts's excellent compilations.[3] Superconductivity was first observed in elements, and this experience led the way to higher transition temperatures in binary intermetallics. Our work with these systems leads us to conclude that the only genuine hope of going to even higher temperatures lies in turning our attention to ternary systems.

Here we will limit the discussion to two groups of superconductors: The elements and the (relatively) high-transition-temperature compounds. Elements are essential to a conceptual understanding of the occurrence of superconductivity, while only those compounds with high transition temperatures and therefore high critical fields are of interest for technological applications like magnets, motors, and transmission lines.

## Superconducting elements

Until the early 1960's the superconducting elements were a minority among all metallic elements. Consequently, superconductivity was considered to be an anomalous property. Since then so many new elements have become superconducting, at lower temperatures or higher pressures, that by now most metallic elements are superconducting. Thus the question has reversed from, "Why do some metallic elements become superconducting?" to "Why do not *all* of them become superconducting?" In figure 1, the superconducting elements are shown by the colored squares. When the square is half filled, the element becomes superconducting only under pressure, or in thin films condensed at liquid-helium temperatures or at temperatures so low (as in the case of rhodium, 0.2 millidegrees Kelvin) that at present the critical temperature can be determined by extrapolation only. When it became evident that in addition to bismuth, tellurium also became superconducting under pressure,[4] it was suddenly apparent that all nontransition elements




**Superconducting elements** in periodic table of the elements.
Figure 1

in this part of the periodic system, once they became good metals under pressure, would also become superconducting. Soon afterwards, the superconductivity of antimony was also discovered.[5] Thus, as early as 1965, the superconductivity of selenium, germanium, arsenic and phosphorus were predicted.[6] Since then, all these elements have been found to be superconducting.[7–10] J. Wittig, who discovered most of the superconducting elements under pressure, has recently found superconductivity in cerium, barium, yttrium and cesium.[11–13] The superconductivity of cesium dispels for the first time in a decisive way the theoretically derived myth that the alkali elements could show the effect only in the microdegree range. Thus, generally speaking, most metallic elements will become superconducting except when magnetic ordering interferes. When I first expressed this opinion, at the Colgate Conference, it was met with laughter and assurances that alkali metals would never become superconducting.[14] Since Wittig's recent discovery much of this laughter can no longer be heard.

Recently, in a review article of our high-pressure data,[15] the conclusion was reached that in elements such as zinc and cadmium superconductivity would eventually disappear at very high pressures. In my opinion, this is a rather naive conclusion based on data below 30 kbar that were then extrapolated to 200 kbar. There will always be new modifications at higher pressures with higher transition temperatures, just as the temperatures for tin and bismuth initially decrease with pressure but eventually rise again to 7 K and above. After all, 25% of the superconducting elements are superconducting above $10^{-2}$ K *only* under pressure. Many elements have become superconducting under pressure, but none has ever lost this property yet!

For the nontransition elements the transition temperature never exceeds 7 K and is fairly independent of the specific electron configuration. Among the transition elements, the maximum transition temperature occurs for niobium at 9.5 K, and technetium at 8 K. Aside from a few exceptions, maximum transition temperatures for the transition elements and their solid solutions always occur when the average number of valence electrons per atom ($e/a$) is near 5 or 7. For lanthanum, which has only three electrons but has a virtual or low-lying 4f configuration, the transition temperature can be raised from 6 K to above 12 K by the application of 140 kbar of pressure.[16] Thus lanthanum (along with uranium, which has an equivalent 5f situation) is exceptional.

## Solid solutions

The precise locations of highest transition temperatures in solid solutions vary somewhat from one crystal structure to the next, because the maxima and minima generally do not coincide with a specific element. Instead, solid solutions with neighboring elements determine much more precisely the exact locations as well as the maximum obtainable transition temperatures in these regions. The maxima as a function of $e/a$ are somewhere between 4.6 and 4.8, and then again between 6.4 and 6.7. Nb–Zr with a transition temperature close to 12 K and Nb–Ti with a transition temperature slightly above 10 K are the best examples for the low $e/a$ side. Mo–Tc compounds with transition temperatures near 14 K are the optimum situation for the high $e/a$ ratio. However technetium still costs about \$100 per gram, and while cubic Mo–Re with a transition temperature exceeding 11 K is one of the most ductile materials known, it is not superconducting in fields above 20 kilogauss. Consequently, Nb–Zr and Nb–Ti have become technologically the most important superconducting materials when one is limited to only the ductile solid solutions. They are, in contrast to intermetallic compounds, quite ductile, and wire made from them is therefore much easier to use. While the critical current densities are between $10^5$ and $10^6$ amp/cm$^2$, the critical fields hardly ever exceed 180–190 kilogauss. Nb–Ti is advantageous for high current densities, while Nb–Zr will withstand higher critical fields.

In superconductivity, just as in ordinary metallurgy, alloys consisting of several elements are generally better suited for specific applications than alloys composed of only two elements. For wires made of ductile alloys, solid solutions of elements with an average valence-electron concentration per atom of between 4–5 or 6–7 are the only choice we have at present. The most perfect solid solutions are of course usually formed by neighboring elements. Throughout the whole range of the transition elements, with one exception, solid solutions are the only stable combinations ever formed by neighboring elements. The one glaring exception of this rule is the relation between the elements of the sixth and seventh columns. Here neighboring elements, besides forming extensive solid solutions with one another, do combine in several well defined intermetallic compounds, the crystal structures of which are quite different from those of their constituent elements. They belong to three different structure types: the $\alpha$-Mn, $\beta$-W, and $\sigma$ structures. Nearly all compounds in these structure classes whose $e/a$ ratios are between 6 and 7 do become superconducting. The formation of these compounds between neighboring elements, for example, Mo–Tc and W–Re and the nonsuperconducting Cr–Mn is, as pointed out before, restricted to these two columns and cannot be found anywhere else among the transition elements. This unique and intriguing feature indicates immediately the crucial role of d-electrons for high superconducting transition temperatures.

While the current band picture is unable to explain this behavior, one can readily understand it on the basis of a bond picture. In the sixth column, the d-shell is half filled and hence quite stable. It is the most stable configuration after a filled shell. Any increase in the number of d-electrons will considerably disturb the stability of this half-filled configuration. It is now easy to see why there are two maxima for the superconducting transition temperature (see figure 2). The more d-electrons or holes, the higher the transition temperature, and if the half-filled shell would not intervene, the sixth column would have had the only (and probably much higher) maximum in transition temperature. But instead, the semistability of the half-filled shell appears as the decisively interfering factor.

### Intermetallic compounds

While the formation of compounds between neighboring elements is thus severely limited, large numbers of intermetallic compounds are formed once the elements are no longer nearest neighbors in the periodic system. The number of intermetallic compounds that are combinations between metals and metals, or between metals and nonmetals, is very large. They crystallize in many different crystal structures, and a great many of them are superconducting. The variation of transition temperature with the average number of electrons per atom is again very pronounced, but no longer as clear cut as for the elements and their solid solutions. In particular, for different structures the maximum transition temperatures now occur at quite different electron concentrations. However, high temperatures are again limited to a few crystal structures, almost all of which are cubic.

The prototypes of these structures are:

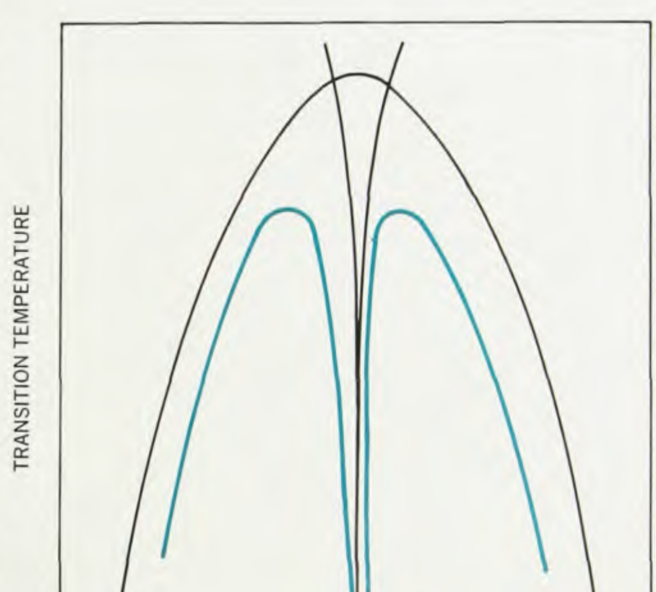
| | |
|---|---|
| $\alpha$-Mn | $\beta$-W |
| NaCl | $Pu_2C_3$ |
| $\beta$-Mn | $MgCu_2$ |
| $\sigma$-phase | |

The superconducting behavior as a function of electron concentration throughout these crystal systems is extremely well described in Ben Roberts's compilations[3] and other recent accounts.

Just as for the elements, the transition temperature is determined essentially by the average number of valence electrons per atom. However, the actual curves are now quite different. In $\beta$-W there are still two maxima, (see figure 3), but at electron concentrations different from those in the elements. In the face-centered cubic NaCl structure (see figure 4), only one maximum exists, and the variation of transition temperature is the same as that of the face-centered cubic elements.[17] The $e/a$ ratio for maximum transition temperatures in the latter two structures is still near 5. In the $Pu_2C_3$ structure, there is again only one maximum, but $e/a$ is now slightly below 4.[18] Other structure types such as the $MoB_2$ or $ThSi_2$ show this same behavior of a peak for the transition temperature at $e/a$ slightly below 4, but their transition temperatures never exceed 13 K.[19]

### High transition temperatures

Transition temperatures above 12 K are found only in the $\beta$-W, NaCl and $Pu_2C_3$ structures. At present it is impossible to find any common feature between these different structures, except for two facts: They are all cubic, and their lattice constants are not too large, that is, not above 10 Å. At present, of all three groups, only one compound in the $\beta$-W is of importance in its technological applications. It is $Nb_3Sn$ (18 K) discovered in 1954 at Bell Telephone Laboratories. While this compound is intrinsically a very brittle substance, research on varied methods has succeeded in combining it with a ductile base of niobium metal. Mag-




**Stability** of half-filled d-shell interferes with superconductivity. Parabola represents total number of d-electrons or holes, colored curves are transition temperatures. Figure 2 nets wound with these $Nb_3Sn$ composite ribbons easily reach fields in the vicinity of 150 kilogauss.

For many years, $Nb_3Sn$ was also the superconductor with the highest known transition temperature. During the last few years, however, this temperature was raised to 21 K by the formation of the pseudobinary β-W compound;[2,20]

$$Nb_3(Al_{0.75}Ge_{0.25})$$

The critical field of this compound is above 400 kilogauss at liquid-helium temperatures.[21] No magnets have yet been built with it, but it is already clear that magnets of 200 kilogauss and above will eventually be available in the same way that 100 kilogauss magnets can be easily bought today, though they are still rather expensive. Raising the transition temperature of a binary compound by adding a third element has been achieved earlier in the other two structures: NbN at 16 K was raised to 17.8 K by forming Nb(N,C), and $Y_2C_3$ at 14 K was increased to 17 K in the ternary compound $(Y, Th)_2C_3$.[18]

The increase of the superconducting transition temperature and the discovery of new superconductors in the range above 12 K has been a very slow process, and has so far occurred in only three places: Bell Telephone Laboratories, Los Alamos Scientific Laboratories, and the University of California in La Jolla. This is rather surprising in view of the ever increasingly important role superconductivity plays in the field of electric technology. What are the factors responsible for this slow progress? First, it is not easy to raise the superconducting transition temperature because the metallurgy involved gets increasingly complicated. Furthermore, there seem to be intrinsic obstacles to high transition superconductors. And last, but not least, the theory has failed to show us what direction to follow. To date, it has only succeeded in leading the experimentalists astray.

Experimentally we have found that with elements alone, a maximum transition temperature somewhat above 12 K can be reached. With binary compounds, the vicinity of 18 K seems to be the current limit. And through the formation of pseudobinaries with a third element, another increase of 3 K seems to be all we can reach at present in the three favorable groups. Undoubtedly, the transition temperature of $Nb_3AlGe$ will eventually be raised by the addition of more elements, but I don't think that the increase will be more than a degree or two.

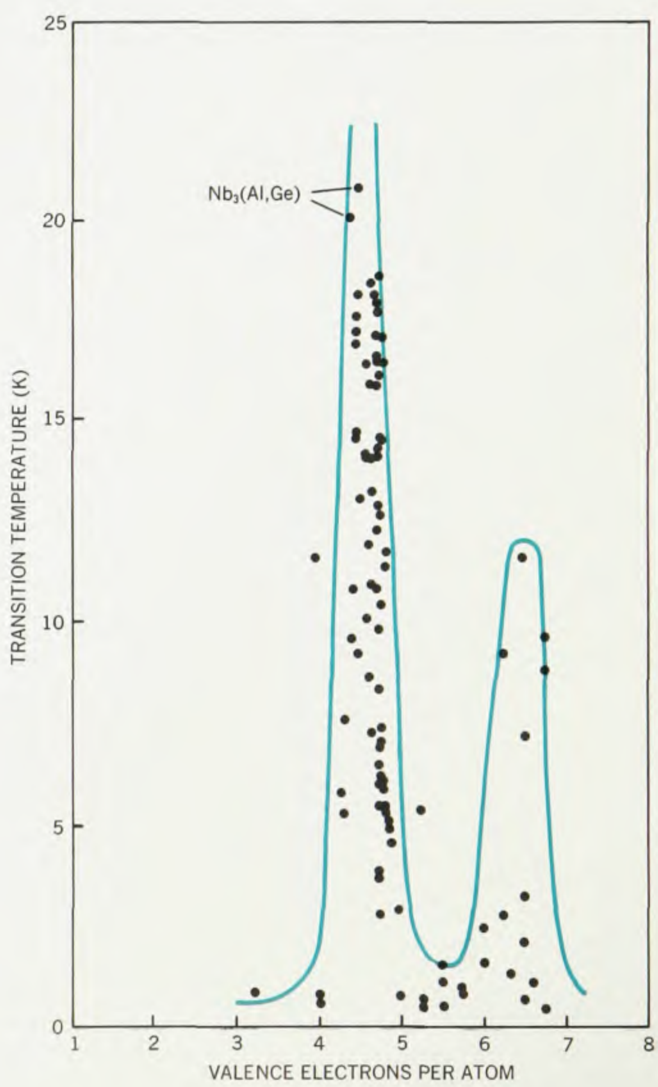
Soon after the empiricism for high transition temperatures had been formulated in 1954, it became evident that there is a distinct aversion in nature to form intermetallic combinations with elevated superconducting transition temperatures. If any did form, they were not very stable. For example the highest transition temperature of lanthanum and $V_3Si$ above 12 K and 18 K respectively, were found only under pressure. Nature's aversion to high transition temperatures, as displayed by instabilities, can take on many forms. Only by avoiding them through relying on the metastability of high-temperature phases will we be able to raise transition temperatures in the future. Let me illustrate this thesis for the three best known crystal structures: β-W, NaCl and $Pu_2C_3$.

**β-W:** If we could synthesize $Nb_3Si$ or $Zr_3Sb$ in the β-W form their transition temperatures might be higher than any known at present. These compounds crystallize instead with an *a*-axis of the correct dimensions for the cubic symmetry but a *c*-axis that is almost exactly twice the value of the *a*-axis. This structure is now tetragonal and no longer superconducting above 1 K. When high transition-temperature compounds do form in the β-W structure, such as $Nb_3Sn$, $Nb_3Al$ or $V_3Si$, they are no longer stable at the superconducting transition temperature. They usually undergo a martensitic transformation at temperatures above the superconducting transition. The structure is again now tetragonal, but with a $c/a$ ratio very close to unity. Consequently, the superconducting transition no longer disappears entirely but is lower by 6–10 K than for the cubic modification.[22]

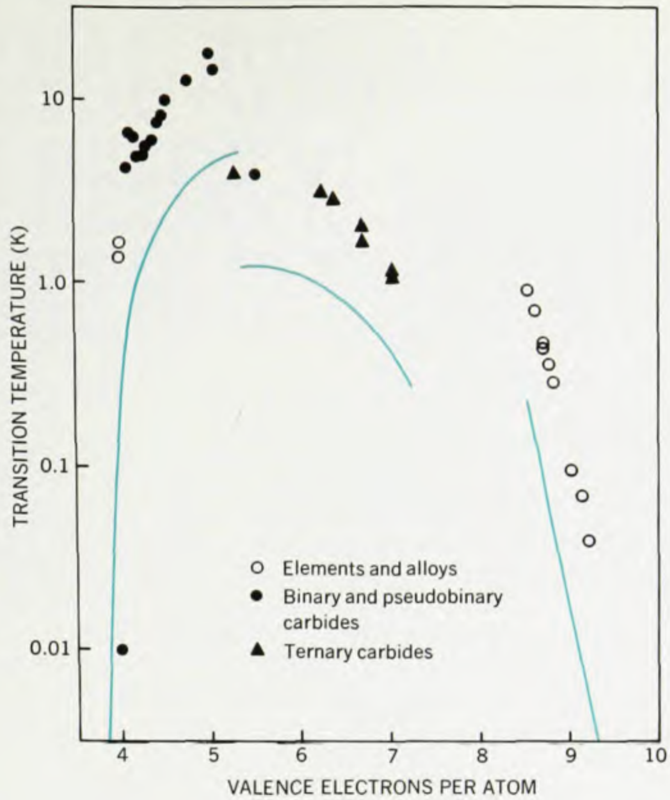
**In the $Pu_2C_3$ structure** a combination of high pressures and high temperatures is required even to form most of the compounds.

**And in the NaCl lattices** the interstitial compounds hardly ever occur in the correct, or stoichiometric 1:1, ratio; any deviation from this ratio results in a precipitous drop of transition temperature.[23]

New methods of low-temperature synthesis, improved annealing techniques for increasing the ordered ar-




**Transition temperatures** versus valence electrons/atom for β-W type compounds. Figure 3




**Superconductivity** in transition-element, face-centered-cubic structures. Maximum transition temperature occurs near $e/a = 5$. Figure 4

rangement, and a continued emphasis on the discovery of cubic structures following the $e/a$ conditions outlined above will definitely raise the superconducting transition temperatures further. At the same time, the instabilities will increase further and will have to be overcome by relying on the metastability of the high-temperature phase.

Those who have been unwilling to accept the necessity of dealing with these instabilities have had problems of their own. Organic structures with preferred directions have been advertised as possibly superconducting at room temperatures.[24] Here the stumbling blocks have become now clear and evident. The compounds, instead of becoming superconducting metals, turned into ferroelectric semiconductors[25] as had to be expected for arrays with a single preferred direction. Once upon a time, high-temperature superconductivity was also anticipated in hot, dense plasmas.[26] However, long before these hypothetical states had been achieved, the systems had ceased to be stable. Then it was found that aluminum films became superconducting somewhat above 5 K compared to the bulk temperature of near 1 K. Eventually the theory[27] predicted much higher transition temperatures, ranging from 28 K to 40 K for thin films of different elements. Yet none has yet approached the aluminum enhancement of even 6 K.

So much for the experiments that failed. The exciton theory, appearing in annual installments[28] seems to have already been disproved theoretically.[29] So far there hasn't even been an experiment. It is all really quite distressing!

The essence always remains the same: As had been anticipated more than 20 years ago,[30] the lattices of high-transition-temperature superconductors are unstable. This was one of the conclusions reached soon after John Bardeen and H. Fröhlich had discovered the electron-phonon interaction as one of the mechanisms causing superconductivity, and many experiments have since confirmed this apprehension. We might expect that, given such initially successful theoretical prediction, the theories of these last 21 years should have also been able to show a way (if one exists) to increase the critical temperature. But until this day there has not been a shred of evidence for this expectation. I can think of no other field in modern physics in which so much has been predicted without producing a single experimental success. Especially since 1957, with the advent of the Bardeen-Cooper-Schrieffer (BCS) theory many hundreds of papers and learned treatises have appeared, describing and predicting superconductivity at elevated temperatures, at room temperature, and even above. And yet, these papers have not led to a single success in raising the transition temperature. The deluge of idle speculations coming to us these days from all sides just won't do it—all it will manage to do is to widen the credibility gap instead of the energy gap. In the spirit of our times, there is an increasing tendency to substitute for nonexistent results many words of great expectations.

Descriptions and explanations of superconductivity in the framework of BCS theory is a beautiful approach in the right hands. Gradually, however, the development has acquired features strongly reminiscent of Goethe's Sorcerer's Apprentice:

*Herr, die Not ist gross*
*Die ich rief, die Geister*
*Werd ich nun nicht los.*
[or]
Master,
Great is my distress today
The ghosts that I have summoned
Just will not go away.

* * *

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