Superconductivity Theory Applied to the Periodic Table of the Elements

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Abstract

The modern theory of superconductivity, based upon the BCS to Bose-Einstein transition, is applied to the periodic table of the elements, in order to isolate the essential features of high temperature superconductivity and to predict its occurrence within the periodic table. It is predicted that Sodium-Ammonia, Sodium Zinc Phosphide and Bismuth (I) Iodide are promising materials for experimental explorations of high temperature superconductivity.

Introduction

The purpose of this talk is to bring to the attention of the experimental community some recent theoretical results of modern superconductivity theory, in a manner which is understandable to those not well versed in the mathematical and physical machinery of this modern day theory. I will begin by explaining in simple, rather naive terms, the essential nature of the modern theory of high temperature superconductivity, which is regarded as a crossover transition theory between the BCS theory of the cooperative Cooper pairing of high-density, weakly-coupled, wide-band electrons, and the formation and Bose-Einstein condensation of low-density, strongly-coupled, narrow-band bipolarons, which is now commonly referred to as the Ogg-Schafroth theory of superconductivity [1-4]. I will then describe to the experimentalist what this new theory predicts concerning the properties of a typical high temperature superconductor, and I will present several likely candidates for materials which are predicted to satisfy those requirements. I will also present a brief but thorough reference list to the theoretical and experimental literature, for those who may wish to pursue an endeavor which I believe will ultimately lead to practical and efficient high and/or near room temperature superconductivity, at the device and product levels.

There is nothing mysterious about high temperature superconductors. The only mysterious thing about theories of high temperature superconductivity are the theorists themselves. It has been said, and not unkindly, that there are as many theories of high temperature superconductivity as there are theorists, that superconductivity theorists do not read one another's papers, that they don't perform experiments and that they never make predictions. Fortunately, they do occasionally publish papers, and many of them are quite good reading. I think the major problem with these theories of high temperature superconductivity is that, as with the theorist, they are usually over-specialized. What we need then, is to identify the most general theory of high temperature superconductivity, which contains the many other theories as special cases, so as not to refute any one theory, thereby offending the theorist. This is precisely what I have done, and in doing so I have obtained a very good theory of high temperature superconductivity, not my own, which is evidently capable of making predictions, which are, ***in theory***, experimentally verifiable.

This new theory of superconductivity is the BCS to Bose-Einstein transition theory and the high temperature superconductivity appears in the crossover regime between these two extremes of this spectrum. The ultimate predictions we would like to make with this theory, are the specific compounds and crystal structures which would ideally demonstrate this wonderful and interesting phenomenon of high temperature superconductivity. If the realization of room temperature superconductivity is ever to come about, we must move beyond the notion that the heavy metal/alkaline earth/copper oxide/layers are the ultimate manifestation of the concept of high temperature superconductivity. We must think boldly. It does not suffice to perform endless experiments with no theoretical understanding of the basic phenomena, nor does it make sense to create individual theories which are incapable of making predictions, and are not experimentally verifiable. To truly know about high temperature superconductivity, we must be at one with the periodic table of the elements.

The appeal of the BCS to Bose-Einstein transition theory lies in its simplicity and elegance, and also its ability to give exact results in the BCS and Bose-Einstein extremes, as well as meaningful results in the crossover regime. It also pays tribute to its predecessor in that it lends credibility to the original Ogg-Schafroth theory of superconductivity, yet the generalization of the BCS wavefunction is still equally valid in both extreme limits. It is only in this crossover regime, dominated by fluctuations, and ultimately, phase separation, where the application of Migdal's theorem becomes invalid [5], and the bipolaronic effects become dominant. This is precisely the regime we are interested in, where charge, spin and mass degrees of freedom couple in extraordinary ways, producing the enhanced electron lattice interactions, creating what we now know as high temperature superconductivity. The ability of this theory to yield useful predictions lies in the fact that, while this theory encompasses a ***continuum*** of models from one extreme to the other, we now know that the occurrence of superconductivity in the crossover regime involves only electron pairs, and thus the application of this theory to the periodic table of the elements in this regime, requires that the model be ***discrete*** within the ionic lattice, up to the correlation length. As we shall see, this implies that severe constraints exist on the geometry and composition of the lattice, and thus, this greatly simplifies the choosing of the elements for the optimum superconducting effect. By process of elimination then, we quickly arrive at the results.

Results

The experimental results which verified the BCS to Bose-Einstein transition theory as the correct approximation of the thermodynamic description of superconductivity was the now famous Uemura plot [6]. It was well known at that time that these materials were extreme type II superconductors with extremely short correlation lengths, and by this time the early theoretical results were in place [7-11], but it was the Uemura group's elegant measurements of the energy scales and penetration depths, and the graphical interpretation of those results, that had such a profound impact on the theoretical work in the crossover regime [12-21], and even they were able to correctly point in the right direction at that time [22,32]. The model of this theory has evolved to such a high degree of simplicity in the one-dimensional form, that it is nothing less than beautiful [23-29]. We now have even a more vivid confirmation of the essential enhancement of the electron lattice interaction in the crossover regime, in the form of the simple and elegant simulations done by the Egami group [30-31], and they also are pointing again in the right direction. If there ever was a smoking gun, then this is it. There is no question that the BCS to Bose-Einstein transition theory is the approximate thermodynamic description of superconductivity, independent of any specific pairing interactions, and the enhancement of the electron-lattice interaction by the strong electron/ion correlations within the crossover regime is the essential mechanism responsible for the phenomenon of high temperature superconductivity, as we know it.

The crossover regime is less amenable to theoretical treatment than the extremes, however, and to gain a useful understanding we must again revert to our models, which ultimately have to be verified by experiment. The models come in a variety of forms, but one of the most easily understood forms is the boson-fermion model [32-36], which is also referred to as the bipolaronic two-component model, and the induced pairing model. The motivation for this model is rather simple. Although the continuum theory, for which the one dimensional example is exact, predicts a continuous transition from the fermionic BCS extreme through the bosonic Bose-Einstein extreme, within the crossover regime it is paradoxical, because we must consider the discreteness of the constituent electron pairs. Thus, the only way to satisfy this discreteness condition is to acknowledge that both pair breaking and pair formation interactions are in direct competition with each other. It is precisely this knowledge, coupled with the short correlation lengths and modified energy scales, which allows us to make useful predictions, for not only are the individual electron pairs discrete, but so are the ions which comprise the lattice. Thus, we are able to use the theory as a useful guide in measuring the electron-lattice interaction and coupling strength, and furthermore, we can use dimensionality considerations as a guide to crystal structure.

The theory itself is exact in one dimension [29], and we are now finding that the theory is, in certain respects, analytic in the limit of infinite dimensions [37-44], and these results also apply to the various models. Of course, the dimensions of interest are 2 and 3, [45-47] and these dimensions may be regarded as analogous to the crossover regime. The analysis will be restricted, however, to the one dimensional case, as this is the simplest, but more to the point, we can construct higher dimensions from the lower dimensional cases, and we know the essential BCS singularity is ***not*** unique to the two-dimensional case [24].

The modeling of the BCS to Bose-Einstein transition theory in one dimension is straightforward [29]. The essential parameters here are simply the correlation length of the pairs, and the average interparticle separation, determined by the number density. It is the ratio of the correlation length to the average interparticle spacing, which determines the energy value of the coupling constant, and when this ratio approaches unity, we can then apply the discreteness condition, and derive the strength of the electron-lattice interaction in relative (dimensionless) units. If critical transition temperature correlates directly with the electron-lattice interaction strength, then the only parameters of the problem are the correlation length and number density, and these are obviously discrete in the crossover. The only further complication (or restriction) to this problem, is in the crossover regime. By definition, there are two components, bosons and fermions, each presumably with their own correlation lengths and number densities. But since the ratio of the correlation length to the interparticle spacing is close to unity, then these values are related by the coupling strength, which scales proportional to that ratio. Thus, the complication is a simplification and it is then rather easy to derive a finite number of discrete possible configurations, determined by the relative electron-lattice interaction strength, which also scales discretely in the crossover. In real (bipolaronic) systems these will correspond to on-site, inter-site, and next-nearest-neighbor interactions, also referred to as the microscopic coherence cells.

It is the discreteness of the ionic lattice which simplifies the problem and makes the analysis possible. Since the electrons are nearly localized, then either they are localized, and thus correlated, or they are not localized, but have a finite correlation length, which is measured in units of the lattice constant. Either way, there are only a finite number of possibilities, when the correlation length is short. Thus, it is easy to see that the crossover transition, corresponding to a ratio of exactly unity, represents the maximum density that a bosonic system can remain purely bosonic, and the minimum density that a fermionic system can remain purely fermionic, and that this density is directly proportional to the interaction strength [14], and clearly favors the symmetric formation and/or dissociation of electron pairs, over the units of the lattice constant. The only other parameter is density, and this is what Uemura has been telling us all along. There is nothing mysterious about it.

Therefore, since crossover transition is equivalent to Bose-Einstein condensation, then density of the electron pairs is the primary enhancer of critical transition temperature. In order to increase this density, we must reduce the correlation length, and enhance the electron-lattice interaction, whatever the cost. The cost is great for higher and higher T_c's. As we might expect, the restrictions implied by the discreteness of the ionic lattice also imply that the critical transition temperatures will also scale discretely, and the number of compounds and crystal structures which are able to satisfy the severe constraints implied by the discreteness condition will become fewer and fewer as T_c's climb higher and higher. In fact, unless the charge carrier concentration varies continuously across the transition, we would expect that tripling and doubling behavior of the T_c's would be observed in the crossover region, and this is what is observed. Ultimately, at the maximum theoretical T_c, competition from charge, spin and mass density fluctuations would become so extreme, that the ability of the superconducting ground state to overcome these fluctuations would finally fail, leading to density disproportionation and/or a liquid-gas phase separation [48].

Conclusions

We can now proceed with the application of the BCS to Bose-Einstein transition theory of superconductivity, to the periodic table of the elements, to enable us to predict the nature and occurrence of high temperature superconductivity within the periodic table. As I have stated earlier, we proceed initially by process of elimination, as we already know a great deal about most of the elements and compounds comprising the periodic table. We will use previous experimental evidence in the literature as our guide, but we now know that what we are looking for is something very new, or something previously overlooked, otherwise the cuprates are indeed the final word on high temperature superconductivity, and this exercise will have been in vain. We must understand that, since these materials are in the fluctuation regime when they are in the crossover region, and that the density is the fundamental parameter, then any element or compound may be forced into this behavior, merely by expanding or contracting the lattice [49]. What we are looking for, are materials which induce the largest reorganization of charge, spin or mass, with the smallest variation of the lattice density, that is, materials with the largest electron-lattice interaction strength, which is still less than, or equal to, the disproportionation energy of the lattice [50-52].

The first thing we realize is that most of the existing forms of high temperature superconductivity are not exactly on the crossover transition, because their correlation lengths are several times their interparticle spacing, or their interparticle spacing is several times their interatomic spacing, and they need to be doped into superconductivity. Thus, there is ***some*** room for improvement. It is also obvious that the cuprates are on the BCS side of the transition, that is, the boson/fermion ratio is asymmetric in favor of fermions, and the bismuthates are clearly on the Bose-Einstein side of the transition, asymmetric in favor of the bosons. We observe that the cuprates favor two-dimensional spin fluctuations, and that the bismuthates favor three-dimensional charge fluctuations. Given the fact that, other than T_c, the superconducting properties of the cuprates are poor, and except for T_c, the superconducting properties of the bismuthates are excellent, while their density of states at the fermi level is rather low, then it is obvious that the bismuthates need to be examined much more closely, for possible T_c improvement, and this is what I have done.

We understand that when a material is exactly on the crossover transition, then it is either an antiferromagnetic insulator, if it is linear, or it is a spin singlet superconductor. Another possibility, which has been previously overlooked, is that it may be a diamagnetic insulator, if it is disproportionated, but not actually phase separated. An example of this would be the mixed-valance compounds. In fact, as we now consider the ions within the same theory as the electrons, then a variety of situations emerge, most of which involve ionic pairing states and the geometry of the lattice. Thus, we would expect that, within the crossover regime, pairing states would be extremely sensitive to geometry of the lattice, and that the optimum (extreme) fluctuation states, exactly at crossover transition, would occur when the lattice geometry is metastable, but constrained, by the conditions imposed upon it. Since these pairing states are indeed fluctuating, then the geometry ***must*** be linear. And, in fact, we do observe that the highest critical transition temperatures are obtained, when the cuprate layers are exactly flat, and when the bismuthate lattice is precisely cubic.

We also observe that high temperature superconductivity is often associated with lattice phase transitions, and that these phase transitions occur, not in the superconducting phases, but at their boundaries. It would be easy to imagine that these phase transitions have no relationship at all with the superconducting phases, but the evidence now suggests that these transitions occur at the boundaries of the superconducting phases, precisely because the effect of the superconductivity is to defeat or frustrate these phase transitions. Thus, the theory predicts that at the exact point of crossover transition, at the maximum theoretical T_c, a phase transition from a diamagnetic or antiferromagnetic insulating state, directly into the singlet superconducting state would be observed, independent of doping, and that this transition would be strongly dependent upon density. Thus, the condition of maximum theoretical T_c is a cusp-like phenomenon, and we would expect that, although every element or compound within the periodic table is intrinsically capable of entering the maximum fluctuating state, only one compound is capable of sustaining that state as the highest temperature superconducting state, for any configuration of bosons and fermions.

High temperature superconductivity is a two-component phenomenon involving pairs of electrons and ions within a discrete lattice. When we approach the periodic table of the elements in search of new and better forms of high temperature superconductivity, we can immediately rule out the vast areas inhabited by the metals and intermetallic alloys, because they display the traditional BCS form of superconductivity. Likewise, we can also disregard low density materials, as their critical transition temperatures are much too low. This includes the semiconductor materials which exist along the diagonal metalloid band. The BCS to Bose-Einstein transition theory of superconductivity distinctly predicts that ***anionic metals,*** which are on the borderline between ionic, metallic and covalent bonding, are the best possible choices for investigation. We can precisely predict, with this simple theory, that the materials most favorable for this behavior would be multi-valent or mixed valence metal-anion compounds of the highest possible density, which span the metalloid band, perpendicular to it but not on it. The experimental community has so far investigated the metal oxides, sulfides, fullerides and borides. The only part of the periodic table which has not been previously considered viable material for high temperature superconductivity, are alkali-metal and group V-halide salts, and these are precisely the type of materials and compounds which this theory actually predicts, as having the optimum high T_c properties.

There are also only a handful of distinct and discrete methods of moving across the metal-insulator transition occurring at the crossover transition, at maximum theoretical T_c. One method would be to take a high density fermionic metal and then continuously reduce the density, until the pairing interaction at the crossover transition sets in. There is now no question that this is precisely what occurs in Sodium-Ammonia solutions, and this was the original motivation for Ogg's experimental investigations of this system. Another method would be to take a low density bosonic insulator, and continuously increase the density of the bosons, until metallic behavior sets in at the crossover transition. It is my fundamental thesis that this occurs in the bismuth iodide system, and since we are dealing with discrete bosons at the outset, the theory predicts that the exact nature of the transformation is from the diamagnetic insulating state, to the singlet superconducting state, which is necessarily manifested by a polymeric mixed-valance to f.c.c. Bismuth (I) Iodide phase transition [64].

The metal ammonia solutions have been around for a long time, and like the high temperature superconductors, they have been extremely resistant to theoretical description within the crossover regime [53-57]. The relationship between bismuth iodide and sodium ammonia solutions, on the other hand, has been previously overlooked, even though the molten salt chemists have known that there are many similarities in their behavior, and the Russians have been for many years predicting that this system would exhibit precisely this type of behavior [58-61]. If the sodium-ammonia is regarded as a continuous, low density fermionic system and the bismuth-iodide is seen as a discrete, high density bosonic system, then theory predicts that, at maximum theoretical T_c, we would expect to find an optimum mixed boson-fermion system, which would scale across the metal insulator transition in a discrete and continuous manner midway between sodium-ammonia and bismuth (I) iodide. And, in fact, we find that the Russians are again observing that zinc phosphide appears to display these same bosonic pairing states [60-61]. It is only necessary to add fermions to this system, in order to induce this material into the crossover regime, and alkali metal is obviously an ideal way to do this. ***Sodium Zinc Phosphide*** is thus an entirely new system.

As we move away from the metal insulator transition and maximum theoretical T_c, which occurs along the metalloid band within the periodic table, more ionic configurations become possible, and this is where I believe the well known exotic superconductors reside. At maximum theoretical T_c, it is the phase separation and disproportionation of the ionic lattice which must be overcome to produce the high temperature superconductivity. As this temperature decreases, it is expected that less extreme methods of disproportionation would occur and I expect that the organization of the cuprates into two-dimensional layers is one example of this behavior. On the other hand, as this temperature increases, then extreme methods of control must be imposed upon the lattice to prevent phase separation, and force these materials into the high temperature superconducting state. I believe that selective chemical oxidation is one method of accomplishing this, and that reports of high temperature, high current conductivity in oxidized polypropylene and sodium-ammonia are a demonstration of this phenomenon. In fact, if the role of oxygen and hydrogen is seen as the primary mechanism of oxidation and reduction reactions, and the concept of metallic, superfluid hydrogen is considered valid, then it is only a small step to controlled oxidation and reduction reactions in a superconducting environment, at quantum unit efficiency, and a superconducting, sodium-based Castner dry cell might be one result of this technique.

I will conclude by giving a vision of things to come. I have learned a great deal by the application of this BCS to Bose-Einstein transition theory of superconductivity to the periodic table of the elements, much more than I could describe in this short presentation. I believe we are on the verge of a revolution in solid state and condensed matter physics, and that this theory unequivocally predicts the existence of an entirely new class of high temperature superconductors - the inorganic ***metal-salt*** solutions. I also believe that these materials are much more than simply better high temperature superconductors. There are deep relationships between the physics and chemistry of these materials, and the periodic table, and the existence of the liquid-gas phase separations and non-linear interactions, indicating that these materials are more efficient and environmentally friendly alternatives to the traditional physical, chemical and mechanical devices which now dominate our lives.

I openly admit that there is no new science in this report. I have only made an unbiased and common sense application of what appears to be a very good theory of superconductivity, to the periodic table of the elements, based upon the totality of the theoretical and experimental evidence. In this respect, my references are incomplete, thus, I apologize for any omissions from the list. Since it is presently beyond my ***immediate*** capability to carry through the experimental chemistry required to confirm or refute these results, the purpose of this report is to inform those of you who may wish to pursue this endeavor. It is now up to the experimental community to attempt to confirm or refute the specific predictions this theory is able to make. If this theory is correct, and I have yet to uncover any clear evidence to the contrary, while the competing models have all been shown to be generalizable by this theory [62-64], the results should truly be spectacular.

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