

On the Nature of Bismuth (I) Iodide in the Solid State

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Abstract

Bismuth (I) iodide is predicted, from theoretical principles and experimental evidence, to be a unique and distinctive material for high temperature superconductivity and superfluidity, thermomagnetic and thermoelectric energy conversion, the electrolysis of water and the catalysis of hydrogen and oxygen.

Key Words : high temperature superconductivity, high temperature superconductors, thermoelectricity, thermoelectric, metal - insulator transition, boson - fermion model, BEC, BCS, crossover transition, polarons, bipolarons, bipolaronic superconductivity, electronic Bose-Einstein condensation.

The bipolaron theory of superconductivity, developed mathematically by the Grenoble group,¹⁻⁵ and physically by DeJongh⁶⁻⁷ and Emin,⁸⁻⁹ has recently been supported by experimental evidence, in the form of muon spin relaxation experiments by Uemura *et al.*,¹⁰⁻¹¹ for the exotic superconductor families. Although this theory is in a naive state, and the experimental evidence for it is still rather sparse, it is now possible to envision a theory which encompasses the BCS theory of superconductivity, and its associated Cooper pairs, and the bipolaron theory of superconductivity, and its associated bipolarons, as special cases of a more general theory of "Bions",¹³⁻²⁴ which may be considered as mutually (non) overlapping bosons and fermions, depending on their concentration, effective mass, correlation length, and hence, the degree of overlap of their electronic wavefunctions. Given the highly correlated nature of the spin, charge and mass distributions in these systems, it may even be possible to predict the type of materials and compounds which would optimize the conditions for these interactions.

Data¹⁰⁻¹² clearly indicates that the relevant physical parameters in these exotic superconducting systems are the density of superconducting charge carriers n_s , the effective mass of the charge carriers, m^* , the correlation length ξ , the effective Fermi temperature, T_F , which is proportional to the expression $n_s^{2/3}/m^*$, that is $T_F \propto n_s^{2/3}/m^*$, and ultimately, the superconducting critical transition temperature, T_c . Metallic elements and alloys have large T_F 's, derived from their large carrier densities and low effective masses, ($\approx m_e$), with long correlation lengths, and relatively low critical transition temperatures. The exotic superconductors possess low T_F 's, derived from their low carrier densities and/or large effective masses, with short correlation lengths, and relatively high T_c 's. It is clear we must extrapolate from the region of metallically conducting charge carriers, into the region of electron localization and large effective mass.

The μ SR data¹² provides one important experimental fact which must be explained by any viable theory of high temperature superconductivity. This is the fact that the theoretical Bose-Einstein condensation temperature of a gas of non - interacting bosons is proportional to the expression $n_s^{2/3}/m^*$, whereas in these exotic materials, the saturation and suppression of T_c with the increasing value of $n_s^{2/3}/m^*$ is observed, contradicting this result.¹² This particular observation also corresponds to the qualitative relationship of T_c vs T_F derived above. That is, T_c is definitely not proportional to T_F or $n_s^{2/3}/m^*$ in BCS systems.

It is known that superconducting charge carriers are interacting to some degree in these systems, mediated by the ions, and resulting in the overlap of their electronic wavefunctions. If one assumes that at some critical value of the expression $n_s^{2/3}/m^*$, specific in some way to the structure and chemistry of the system, that excessive overlapping of the electronic wavefunctions serves to inhibit the formation or condensation of bosons, then this result is understandable.

The expression $n_s^{2/3}/m^*$ is thus seen as a measure of the degree of overlap of the electronic wavefunctions, and thus, the degree of interactions of the bosons in the system. Furthermore, in order to derive the density vs volume relationships required to (naively) calculate the degree of overlap of the electronic wavefunctions from the expression $n_s^{2/3}/m^*$, the effective mass of the boson must be in some way related to size. I propose, of course, that the effective mass of the boson is inversely proportional to its size, $m^* \propto l^{-1}$, and that size may be roughly measured by the correlation length, ξ .

Approaching the bipolaronic region, the local bosons are only slightly overlapping, and hence, $T_c \propto T_F \propto n_s^{2/3}/m^*$. In order to optimize the value of this expression, we must be familiar with the scaling relationships between n_s and m^* . We have very little information on these relationships, besides Uemura, *et al.*¹² We are thus forced to draw our own conclusions.

Figure 1 - Uemura Plot

One conclusion which may be reached is that, up to localization, the critical transition temperature is inversely proportional to the correlation length, $T_c \propto \xi^{-1}$, and proportional to the effective mass of the charge carriers, $T_c \propto m^*$. It then follows that the effective mass of the charge carriers is inversely proportional to the correlation length, $m^* \propto \xi^{-1}$. To maximize T_F , and thus T_c , under this restriction, then obviously n_s should be as large as possible, without causing excess overlap of the electronic wavefunctions, and the correlation length should be very small; of the order of the intercarrier separation. In other words, the critical transition temperature may be maximized in a material with a high density of superconducting charge carriers of large, yet minimized, effective mass; i.e. - *local bosons or small bipolarons*.

Emin has stated that the mass of a bipolaron is proportional to the mass of the atoms responsible for its formation.⁹ He has searched for bipolaronic superconductivity in boron carbide, a material of low atomic mass, and has obtained a negative result.⁹ According to

Abrikosov,²⁵ we seek a highly polarizable material, with charge carriers of large effective mass. It is reasonably clear that we should not be considering intermetallic alloys if we wish to maximize T_c . Thus, we should search for ionic (anionic) compounds composed of elements with high atomic mass numbers, at the other end of the periodic table.

As one continues to study these systems, a startling conclusion is reached. As the correlation length approaches the intercarrier separation, and the intercarrier separation approaches the interatomic spacing, that is, as the system approaches a state demonstrating ideal local boson transport at a maximal concentration of charge carriers, the physical constraints on the chemistry of the system may become so restrictive, at the maximum theoretical transition temperature, that ultimately, only one chemical system may be able to satisfy the requirements. It is of this author's opinion that the bismuth (I) iodide system may be one such system.

Searching the relevant modern literature²⁶⁻²⁷ leads to the heaviest possible metal halide, which is, excluding radioactive elements, bismuth monoiodide.²⁸ Searching the literature²⁹⁻⁴² reveals that bismuth (I) iodide, BiI, is a remarkable wide gap, narrow band semiconductor with electronic properties which are clearly bipolaronic in nature.³⁷ There is a great deal of information on this system in the liquid state, and it has been synthesized⁴³ and analyzed⁴⁴ in the solid state, but very little is actually known about the physical properties of bismuth monoiodide in the solid state, other than crystal structure, density and phase diagram.

Figure 4 - Phase Diagram of the Bismuth - Iodide System

Consider the nature of bismuth (I) iodide in the solid state. BiI is a mononuclidic, multi-valent binary solution, crystallizing into the stable mixed valence compound $1^{\infty}[\text{Bi}^0_2\text{Bi}^{2+}_2\text{I}_4]$, consisting of infinite, one-dimensional chains of metal-salt polymers, with weak van der Waals forces and stacking faults in between.⁴⁴ The phase diagram⁴⁵ is reproduced in Figure 4.

Bismuth (I) iodide is isotopically pure. The atomic mass number of iodine is 127, the sum of the atomic numbers of bismuth and iodine is 136 and the neutron number of bismuth is 126. The total molecular weight of unpolymerized BiI is 336, and its density is roughly 7 g cm^{-3} . The ratio of the ionic radii of bismuth and iodine is such that, in the liquid state, at a consolute temperature of 725 K, the bismuth ions nearly perfectly occupy the octahedral holes of the pseudo-cubic quasi-lattice defined by the iodine ions. The average valence state of the bismuth is the reduced oxidation state of Bi^{1+} , although the valence of any one bismuth ion may be fluctuating rapidly. The bismuth ions undergo dissolution in bismuth triiodide, BiI_3 , via the reaction $2\text{Bi}^0 + \text{Bi}^{3+} \leftrightarrow 3\text{Bi}^{1+}$, charge disproportionation via the reactions $2\text{Bi}^{1+} \leftrightarrow \text{Bi}^0 + \text{Bi}^{2+}$, and $2\text{Bi}^{2+} \leftrightarrow \text{Bi}^{1+} + \text{Bi}^{3+}$, dimerization via the reaction $2\text{Bi}^0 \leftrightarrow \text{Bi}_2$, polymerization by extension, $n\text{Bi}^0 \leftrightarrow \text{Bi}_n$, and ionization via reactions such as $\text{Bi}^{1+} \leftrightarrow \text{Bi}^{3+} + 2e$ and $2\text{Bi}^0 \leftrightarrow 2\text{Bi}^{1+} + 2e$.

All of these reactions involve local bosons.

The phase diagram of the bismuth (I) iodide system displays a well defined, symmetric immiscibility feature, which provides insight into the equilibrium dynamics of these reactions. The γ -BiI phase just below the melting point displays a metastability feature which may be related to crystal geometry and chemical equilibrium. In other words, the bismuth (I) iodide system undergoes a phase transition which involves not only the physical liquid to solid phase transition, but also electronic and chemical phase transitions which involve the crystal structure, degree of polymerization and the valence states of the bismuth ions. This is supported by the extensive and excellent experimental data on the system.²⁹⁻⁴⁵

The bismuth (I) iodide system is highly anomalous. For instance, with regard to its reference electrodes, tungsten and carbon (graphite), while both elements are inert to bismuth iodide melts, in the pure salt, purely ionic conductivity, with its associated effects, is observed when measured against graphite electrodes,³⁸ whereas electronic conductivity of the order of twice the ionic conductivity, with the associated absence of ionic effects, is observed when measured against tungsten electrodes.³⁶ Additionally, extremely large (Soret) thermal diffusion effects are observed in the bismuth triiodide system.⁴⁰ The conductivity data also shows an anomalous transition from positive to negative thermal coefficients of conductivity at high temperatures in both the pure salt,³⁹ and the metal rich melts.³⁶

Solid bismuth (I) iodide is obtained by long duration annealing of intimately mixed bismuth metal and bismuth triiodide.⁴³⁻⁴⁵ The largest single crystals obtained thus far are measured in millimeters.⁴⁴ The system does not reach equilibrium after melting.⁴⁵ Single crystals of BiI are not obtained by normal thermal quenching of the melts.⁴⁵ Apparently, the immiscibility region from 590 K to 725 K presents a formidable energy barrier, which must be overcome to produce solid BiI by any conceivable thermal quenching process.

Through disproportionation and polymerization, single crystals produced by long duration annealing contain bismuth-bismuth metal-metal bonds, and are not the cubic ionic phase one would ordinarily expect. No polymerization occurs in the melts at the consolute temperature,⁴¹ although solution must be initiated by agitation,³⁵⁻³⁶ and no significant quantities of Bi^{2+} are detected in the melts.³⁵ Thus, ionic solutions consist of evenly dissolved Bi^0 , Bi^{1+} and Bi^{3+} in I^- . On the other hand, BiI in the solid state appears to consist of covalently bonded Bi^0 and Bi^{2+} with a high degree of polymerization.⁴⁴ The γ -BiI phase may be a metastable transition state between these two phases. Any successfully modified thermal quenching process should produce an ionic solid; a metastable, pseudo-cubic, quasi-three-dimensional bismuth (I) iodide, with properties of the ionic liquid, in the temperature range of the solid.

The effective mass of the charge carriers in this system has been calculated as equivalent to that of an iodine ion, ($\approx 127m_p$). This is a very large, but finite, effective mass. The threshold conductivity at the consolute temperature for BiI is roughly $500 \text{ W}^{-1}\text{cm}^{-1}$.³⁶ This is a very large conductivity for a liquid semiconductor. Extrapolation of the conductivity data indicates that this material may be an insulator at the melting point for most concentrations of salt. With the imposition of long range order on the system, the

effective mass may be drastically reduced, possibly by a factor of m_p/m_e , to yield a more reasonable effective mass in the $127 m_e$ range. Doping of the tetrahedral holes of the pseudo-cubic iodine quasi-lattice may reduce this even further. This effective mass is expected to be in the metal-semiconductor transition range. Thus, half of the charge carriers in BiI would be in metallically conducting states, and half of the charge carriers would be in electronically conducting states. This is expected to be precisely the case for bismuth (I) iodide.

Examination of the phase diagram (Figure 4) indeed shows a smooth transition from metal to semiconductor, if one ignores the immiscibility feature roughly centered at BiI, and the conductivity data displays an exponential increase in conductivity with increasing metal and decreasing salt.³⁶ Thus, while BiI exhibits thermally activated conduction in the liquid state, the material may actually be an insulator at the melting point, and may demonstrate metallic conductivity in the solid state, or may be doped into the metallic state. This effect may be enhanced if the crystal structure is depolymerized; i.e. - *bismuth (I) iodide*.

Thermoelectric potentials may also be extrapolated into the solid state.³⁸ For instance, extrapolation of the Seebeck coefficient, a , indicates that a maximum of $220 \mu\text{V/K}$ could occur at 50% bismuth metal at 300 K. If the crystal structure could be depolymerized, that is, as a cubic crystal, this maximum may go as high as $320 \mu\text{V/K}$, at a composition of 67% bismuth; i.e.- bismuth (I) iodide. This assumes that the Seebeck coefficient is roughly proportional to the ratio of the concentration of bismuth-iodide bonding of Bi^{1+} , relative to the concentration of the bismuth-bismuth metal-metal bonding of Bi^0 , which is admittedly an oversimplification. By plugging in the only known value for electrical conductivity, $\sigma = 500 \text{ W}^{-1} \text{ cm}^{-1}$, and the only reasonable value for the thermal conductivity, $\kappa = 4.5 \text{ mW/cm-K}$ (that of iodine) into the equation $z = \alpha^2 \sigma / \kappa$, an unprecedented zT efficiency ratio of 2 - 4 at 300 K is indicated. While these values are undoubtedly in error, the exercise demonstrates that very good thermoelectric and thermomagnetic efficiencies are, in principle, physically feasible for this material.⁴⁶⁻⁴⁷

Interpretation of the phase diagram (Figure 4) and purely chemical methods,^{37,42,44} allows the calculation of the energy required to break the bismuth metal-metal bonds to depolymerize or dissolve the bismuth completely, to produce a hypothetical metastable cubic bismuth (I) iodide, containing no metal-metal bonding, and consisting of wall-to-wall bismuth-iodide bonding of bismuth ions, with an average valence state of Bi^{1+} . This material would be a quasi-three-dimensional crystalline ionic solid with two well defined tetrahedral holes per site, available for doping. Either pure, or maximally doped with hydrogen, this material may exhibit highly correlated site-to-site hopping of local charged bosons; i.e. - *bipolaronic superconductivity*. The Fermi temperature may be in the 1100 K range, the temperature at which the conductivity of the liquid state peaks, and the thermal coefficient of conductivity becomes negative. The density of charge carriers would be the theoretical (for BiI) maximum of $2.5 \times 10^{22} \text{ cm}^{-3}$. If condensation of the local bosons occurs at all in this system, it would occur at the theoretical three dimensional Bose-Einstein condensation temperature, specified by the equation $k_B T_B \approx 3.31 \hbar^2 / m^*$, which

for an effective mass of 27-127 m_e , could be as high as 273 K, which this author regards as the maximum theoretical T_c .

We could further speculate on the electrochemical nature of this material. Consider the hydrogenated semiconductor BiH_2I . With two tetrahedral holes per site, BiI may be a strong hydrogen absorber, if its tendency to oxidize to BiIO is overcome. The material may exhibit ionic conduction of hydrogen ions, in contrast to electronic conduction of bipolarons, depending on the electrode material. The end result would be the electrolysis of water, or reversibly, the catalysis of hydrogen and oxygen. Isolation of this material from the environment may be one prerequisite for this behavior; i.e. - platinum, tungsten, carbon or quartz.

Bismuth (I) iodide is predicted to be a "*unique and distinctive*"²⁶ host material for superconductivity and superfluidity, thermomagnetic and thermoelectric energy conversion, and the electrolysis of water and catalysis of hydrogen and oxygen. The fundamental premise is that a cubic form of this compound, obtained by rapid thermal quenching of the molten phase, under electromagnetic fields and/or hydrostatic pressure, will display the predicted properties.

This prediction is not without precedent, and is not based solely on the properties of bismuth (I) iodide. A certain amount of intuition and speculation has been applied to arrive at the result, since very little is actually known about the physical properties of this material in the solid state. So, for the benefit of the skeptic, additional information shall be provided; to support the conclusion, to motivate continued research into this remarkable compound, to suggest additional avenues of investigation, and to perhaps inspire the experimental community into attempting the rather difficult synthesis of this material.

The bipolaron theory of superconductivity seems to break down in the strong coupling, high density limit. The conventional theory of non-interacting, hard core bosons is not an adequate description of that state of matter. What the bipolaron theory seems to predict, with some degree of accuracy, is that T_c is maximized in a material with equal proportions of bipolarons and Cooper pairs, derived respectively from polarons and free electrons. At the critical transition temperature, the Cooper pairs are expected to decay directly into free electrons of the Fermi sea, whereas the bipolarons are expected to persist. While the superconductivity of both the bipolarons and the Cooper pairs is expected to display the Meissner effect, the energy spectrum of the Cooper pairs would display a gap, but the excitation spectrum of the bipolarons would be gapless. The combined system should display two gaps.

The conductivity behavior of bismuth (I) iodide is somewhat unique.³⁶⁻³⁷ In the cubic form of BiI , the average valence state of the bismuth is Bi^{1+} , but the material conducts via valence fluctuations coupled directly to the high energy optical phonons in the system.³⁷ Thus, according to the conservation of charge, for every local boson transfer from Bi^{1+} to Bi^{3+} , there must be a corresponding double fermion transfer from 2Bi^{1+} to 2Bi^0 . But in this

system, the mean free path of the electrons is expected to be exactly equal to the lattice constant.³⁷

I propose that bismuth (I) iodide represents the limiting case in that it is difficult to distinguish between electrons and polarons, and Cooper pairs and bipolarons, in this system. Thus, the temperature dependent diamagnetism,³⁵ the semiconducting behavior above the melting point, and the anomalous transition to the metallic state at the Fermi temperature, is in complete accord with the extreme limiting case of the bipolaronic theory of superconductivity.

This particular scenario is not expected to be the case for the polymeric crystal structure known to exist in the solid state.⁴⁴ That material is not cubic, and consists primarily of covalently bonded bismuth ions in the Bi^0 and Bi^{2+} states, and is undoubtedly stable. It is also not expected to be the case in pure bismuth metal and bismuth triiodide, as these materials are covalently bonded and ionically bonded, respectively. If the liquid phase could be rapidly quenched from the pseudo-cubic phase at the consolute temperature, through the two phase region, and into a cubic phase in the solid state, without allowing the physical, chemical and electrical disproportionation of the material into its constituents, then this particular scenario could be expected to hold;
i.e. - *bismuth (I) iodide*.

The BCS theory of superconductivity has been highly successful for metallically conducting systems. Yet, the historical roots of this theory⁴⁸ are more reminiscent of the bipolaron theory of local bosons, and was initially developed by another school of theorists, the Sydney group. We now know that the original idea of the existence of local bosons in superconducting systems dates back to Ogg,⁴⁹⁻⁵¹ and his work on the sodium-liquid ammonia system,³⁶⁻³⁷ although the density and temperature of that system are lower, and the circumstances surrounding conduction and local pair formation are more obscure.

Figure 2 - Phase Diagram of the Sodium - Ammonia System

Ogg⁴⁹ wrote in 1946, "*It is postulated the the liquid-liquid phase separation which occurs on slow cooling (upper consolute temperature 232 K) is the device adopted by the systems to avoid the Bose-Einstein condensation, with its unfavorable free energy change.*" "*By sufficiently rapid cooling, it appears that the liquid-liquid phase separation is prevented, and the system becomes frozen and hence metastable in the forbidden concentration region, which is thus characterized by the Bose-Einstein condensation of the trapped electron pairs.*"

This is precisely what is expected to occur in the bismuth (I) iodide system.

I propose the disproportionation energy as the barrier to the formation of bipolarons. This energy may be supplied to the system during quenching, in the form of electric current, magnetic field, and/or hydrostatic pressure. In fact, given the thermomagnetic efficiency of the material, electrical current and transverse magnetic field applied to the system will

establish a thermal gradient via the Ettingshausen effect, suggesting a possible thermal quenching process.

I also note that ammonia is a very good refrigeration medium. It thus appears that ammonia is a low molecular weight analog of bismuth (I) iodide, given the pseudo-halide character of the hydrogen ion.²⁶ One could stretch the analogy further by noting the extreme solubility of ammonia and iodic acid in water, the oxidation potential of periodic acid, the quenching behavior of sodium iodide saturated ammonia solutions, the instability of bismuthine and the proposed diffusion constant of hydrogen in bismuth (I) iodide. I note the density of hydrogen in BiH_4I is precisely that of liquid hydrogen at one atmosphere, BiH_2I being exactly half of that, and the energy density of NH_4I approaches that of dynamite. Superfluidity of hydrogen ions is a distinct possibility in the bismuth (I) iodide. I refer the reader back to Blatt,⁴⁸ and the quasi-chemical equilibrium basis of the BCS and bipolaron theories of superconductivity, for the calculations involved in these concepts.

Finally, I would like to comment on the role that the oxide superconductors play in this new chemical scheme. I generally adopt the views of Wilson⁵²⁻⁵³ concerning the chemical mechanisms of superconductivity in the oxide system, although I believe that high energy optical phonons mediate bipolaron transport in these systems. The oxides appear to be an intermediate chemical system in which the lower carrier density serves to reduce the overlap of the electronic wavefunctions, and the bipolarons are larger, corresponding to the larger correlation lengths in these systems. Since the oxides also melt incongruently, and are heavily doped into superconductivity, it is supposed that these compounds represent a stable means by which partial disproportionation is either prevented or attained. Although the effective masses of the charge carriers appear to be fixed within a given family of oxides, the doping provides a means to optimize the carrier concentration in these systems. Thus, the oxides represent a set of transition compounds which separate the stable, metallically conducting BCS materials from what may be the true high temperature superconductors; the unstable disproportionating compounds which I believe are uniquely represented by the hydrogen, ammonia and bismuth (I) iodide systems. Unfortunately, the low charge carrier densities and the overall complexity of the oxide materials prevents their optimum utilization in many superconducting applications.

In this respect, I note that the charge carrier concentration in bismuth (I) iodide is the maximum theoretically possible for this system. Any amount of doping will serve to reduce the charge carrier concentration in this system. I propose that barium, or the pseudo-halide²⁶ barium hydride, BaH_2 , would be the optimum means of accomplishing this, as that element would trap out pairs of electrons, while still maintaining the high molecular weight character of the material. There is thus a direct correspondence between (barium) bismuth (I) iodide and the bismuthate superconductor, doped BaBiO_3 , and thus the analogy is rather complete.

Directions for further research are clear. Attempts to produce a cubic form of BiI via an electromagnetically activated thermal quenching process are in progress. Experimentalists and theorists take note. The determination of the physical properties of

bismuth (I) iodide in the solid state, will either demonstrate the truth of these predictions, or contradict them. Surely, the possible use of bismuth (I) iodide as a solid state refrigerant alone is compelling enough to justify pursuing the experimental chemistry required to confirm or deny these predictions.

And should these predictions be refuted? It is hoped that negative results could be put to good use. At least we would know where not to look in the periodic table for materials with these particular design specifications, or that these particular properties are not those desired.

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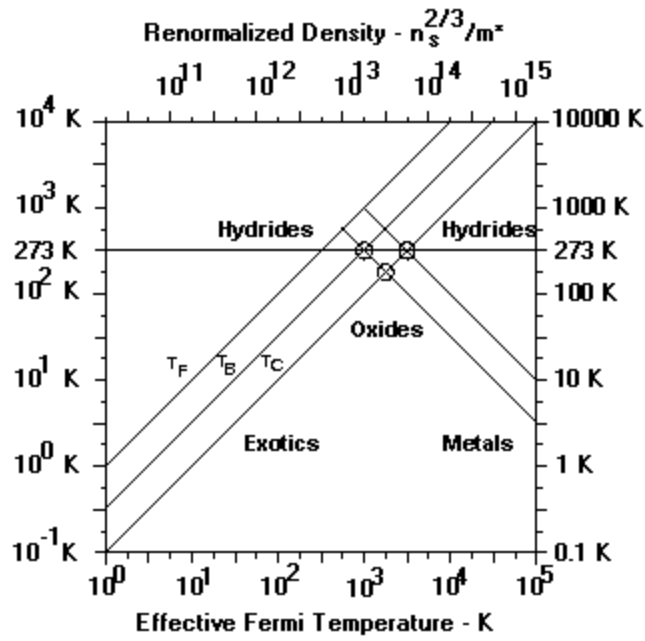


Fig. 1 Uemura Plot (See Uemura 1991 for Details)

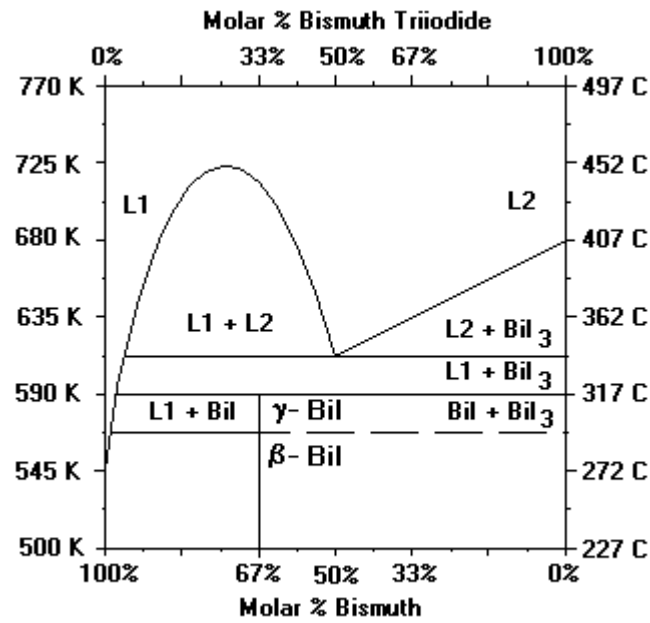


Fig. 4 Phase Diagram of the Bismuth (I) Iodide System

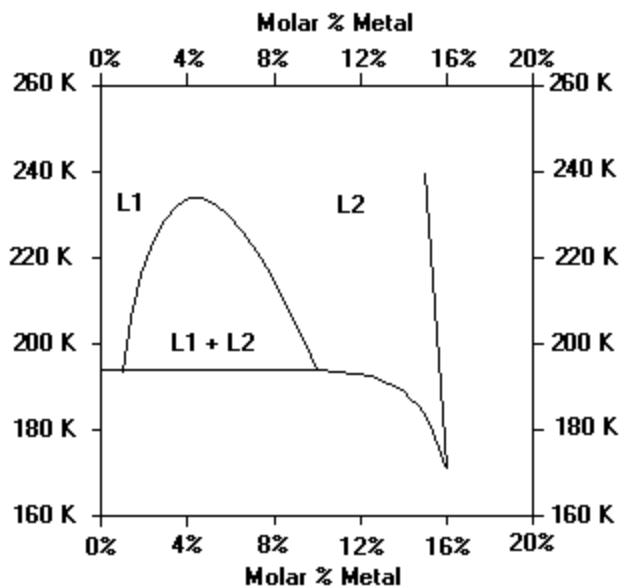
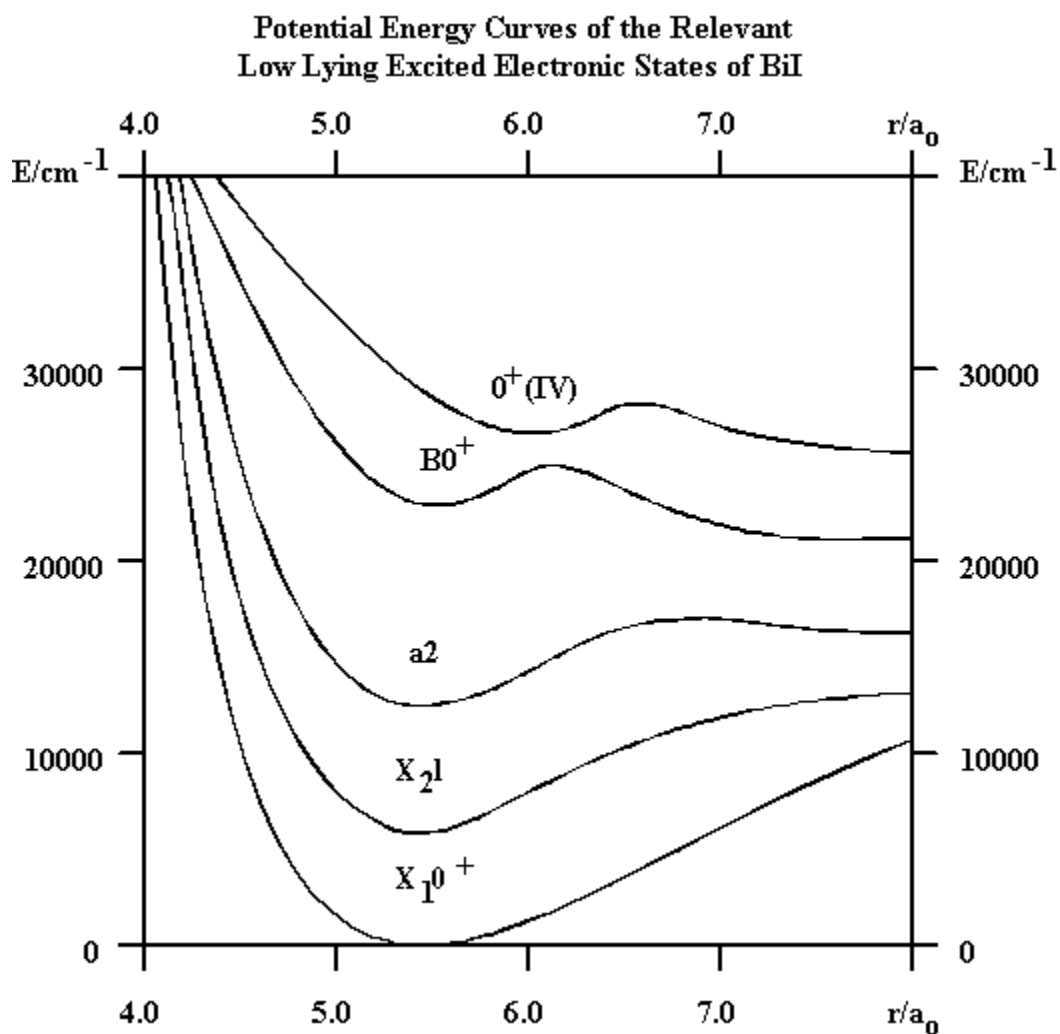


Fig. 2 Phase Diagram of the Sodium - Ammonia System



A Note Added In Proof

This paper provides excellent theoretical descriptions, numerical simulations and experimental verification of the low lying excited electronic states of the bismuth (I) iodide system. It is a striking confirmation of the concept of metastable excited bound electronic states in the bismuth (I) iodide system.

54. Alekseyev, A.B.; Das, K.K.; Liebermann, H.-P.; Buenker, R.J.; Hirsch, G. Chem. Phys. 1995, 198, 333.

The calculated low lying electronic states of the bismuth (I) iodide molecule, compared with the optical and near ultraviolet spectroscopy of the bismuth (I) iodide molecule, reveals that there are indeed two bound singlet excited states, at 2.9 eV and 3.1 eV, the 0+ (III) and 0+ (IV) states, respectively, which actually do span the enthalpy of dissociation of water, at 2.97 eV, and even more remarkably, the equilibrium bond lengths of these two states are 2.9 Å and 3.1 Å, respectively. This opens up the possibility of phonon driven transitions between these two electronic states, to mediate, and then ultimately stabilize, the condensed and superconducting bismuth (I) iodide state.

Table 5. The computed spectroscopic properties of BiI (the excitation energy, T_e , the equilibrium bond length, r_e , and the vibrational frequency, ω_e) together with corresponding experimental data.

State	T_e (cm ⁻¹)		r_e (Å)		ω_e (cm ⁻¹)	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
X ₁ ³ Σ ₀₊ ⁻	0	0	2.886	2.805	156	164
X ₂ ³ Σ ₁ ⁻	5096	6182	2.878	-	152	169
a ¹ Δ ₂	12336	-	2.861	-	155	-
B0 ⁺ (III)	24148	23389	2.898	-	170	198
0 ⁺ (IV)	25691	-	3.095	-	217	-