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High-temperature conventional superconductivity

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Abstract. Conventional superconductors are described well by the Bardeen-Cooper-Schrieffer (BCS) theory (1957) and its related theories, all of which importantly put no explicit limit on transition temperature $T_{\rm c}$. While this allows, in principle, roomtemperature superconductivity, no such phenomenon has been observed. Since the discovery of superconductivity in 1911, the measured critical temperature of BCS superconductors has not until recently exceeded 39 K. In 2014, hydrogen sulfide under high pressure was experimentally found to exhibit superconductivity at $T_c = 200$ K, a record high value which greatly exceeds that of the previous class of high-temperature superconductors, the cuprates. The superconductivity mechanism in cuprates has not yet been explained. Over a period of 25 years, the critical temperature of cuprates has not been increased above 164 K. The paper reviews research on record-high T_c superconductivity in hydrogen sulphide and other hydrides. Prospects for increasing $T_{\rm c}$ to room temperature are also discussed.

Keywords: high-temperature superconductivity, high pressures, hydrides

1. Introduction

Superconductivity represents a state of metal where its resistance is exactly zero, so an electric current can flow at temperatures below a certain critical T_c without losses. Current applications of superconductors are limited and require coolants. Is room-temperature superconductivity theoretically possible? As follows from an understanding of superconductivity phenomenon with the phenomenological Ginzburg–Landau theory [1], the microscopic BCS theory (1957) [2], and some other fundamental theories [3–11], room-

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Received 18 September 2016 Uspekhi Fizicheskikh Nauk **186** (11) 1257–1263 (2016) DOI: 10.3367/UFNr.2016.09.037921 Translated by M I Eremets; edited by A Radzig temperature superconductivity can be realized in a metal with a favorable combination of parameters.

The absence of an upper bound for transition temperature readily follows, for instance, from the Allen-Dynes formula [12]: $T_{\rm c} = 0.182\omega_{\rm ln}\sqrt{\lambda}$, where $\omega_{\rm ln}$ is an average of the phonon frequencies weighted by electron–phonon coupling, and λ is the electron-phonon coupling constant. This formula is valid for $\lambda > 5$, but a more complicated expression for a smaller λ [13] leads to the same conclusion: T_c can be higher than 300 K with a reasonably high Debye frequency and electronphonon coupling. T_c depends linearly on ω_{ln} (while T_c varies as the square root of λ); therefore, materials composed from light elements which provide high frequencies in the phonon spectrum are favorable for a search for a higher T_c [14]. Previous experiments did not support this prospect: in spite of an intensive search, T_c was limited to 39 K (Fig. 1). As a result of the disappointing experimental search, as well as some misinterpretations of the BCS formulae, a strong belief was widely held that superconductivity in metals cannot exist at temperatures above 30 K [15]. This belief was shaken by the revolutionary discovery of superconducting cuprates in 1986 [16], when T_c increased quickly from 30 K to 164 K [17, 18]. But in spite of a 20-year effort exerted by many scientists who turned their attention to these 'unconventional' superconductors, no further progress towards a higher T_c was made. Future prospects are not clear as well, because the mechanism of high-temperature superconductivity in cuprates remains obscure [19].

The recent discovery of superconductivity with $T_c = 203$ K in H₃S compound [20] — an apparently 'conventional' superconductor — turned attention back to the predictions of BCS theory concerning the room-temperature superconductivity. Hydrides are of obvious interest here because hydrogen atoms are the lightest ones and bring the required high frequencies to the phonon spectrum [21].

It is natural to consider first pure hydrogen, as the discovery of high- T_c superconductivity [22] in sulfur hydride stems from the search for metallic hydrogen. Metallic hydrogen is a distinct candidate for high-temperature conventional superconductivity: it exhibits extremely high phonon frequencies ($T_D \approx 2000$ K) and a strong electron–phonon coupling ($\lambda \approx 2$), as was first suggested by Ashcroft



Figure 1. (Color online.) Highest- T_c materials discovered over the years. Unconventional cuprate superconductors are marked by orange squares, conventional ones by blue dots. The arrow indicates 1957—the year of the publication of the Bardin–Cooper–Schrieffer theory. (Taken from Ref. [47].)

[21]. Further numerous calculations confirmed that a T_c of 200–400 K [23–25] can be expected. However, metallic atomic hydrogen is still elusive in spite of significant progress in both theoretical computations and experiments. We note here that in one of the latest experiments a new, probably metallic, phase of hydrogen was achieved under an enormous pressure of 380 GPa [26].

In view of the apparent difficulties in reaching the metallic hydrogen state, Ashcroft [21] proposed that hydrogendominant materials, such as CH4, SiH4, and GeH4covalent hydrides-might transform into metals at much lower, accessible pressures. These substances can be hightemperature superconductors for reasons similar to those for pure metallic hydrogen: a high Debye temperature and a strong electron-phonon coupling. Heavier atoms in the lattice might be beneficial by bringing in low frequencies in the phonon spectrum to enhance electron-phonon coupling. That was a qualitative consideration, but the idea was timely, as it could be examined both experimentally and based on calculated results. The 200 GPa pressure range required for the metallization of many covalent hydrides became reachable (partly due to the 'race' for metallic hydrogen). From the theoretical side, at that time *ab initio* predictions of the crystal structures have been developed [27-30]. They are ideally suited for a search for conventional superconductors: as soon as the lattice structure is determined, the phonon and electronic spectra can be calculated, and then T_c can be estimated from the Migdal-Eliashberg theory [8, 9].

The experimental search at the beginning did not support the expectations of high-temperature superconductivity in covalent hydrides — it was not found in AlH₃ (at least at temperatures >4 K) [31]. On the other hand, the experiment strongly supported the theoretical predictions for highpressure lattice structures in AlH₃: a new high-pressure $Pm\bar{3}n$ phase was found in exact agreement with the independent prediction [32]. This is probably the first example of an amazingly exact prediction of the structure of a new compound. In spite of the correctly found structure, the ordinary calculations of the phonon spectra and the estimation of T_c from the common MacMillan formula [33] were not sufficient. It turned out that anharmonic effects must be taken into account, and it is precisely these effects that are responsible for the suppression of superconductivity in AlH₃ [34]. Later on, anharmonic corrections were considered in other hydrides and found to be significant.

The next experimental study of silane [35] again demonstrated an exact agreement with the independently predicted (I41/a) high-pressure phase [36]. However, the computations were not able to see a metallic, superconductive phase in the 50–100 GPa range. This study demonstrated that transformations in hydrides can be complex and likely accompanied by amorphization [37] and disproportionation [35].

In contrast to a few experimental studies, the theoretical calculations of the covalent hydrides were prolific, with many compounds being examined [38, 39]. In addition to the known pure hydrides, mixtures with hydrogen were also considered and compounds of hydrides stable at high pressures were proposed. They have a very high content of hydrogen and can be considered 'dirty' hydrogen. Very high $T_c \approx 240$ K was predicted for CaH₆ [40], $T_c = 264$ K in YH₆ [41], $T_c = 102$ K in GaH₃ [42], and $T_c = 146$ K in AlH₃(H₂) [43]. These calculations are very encouraging and motivate further experiments. Unfortunately, most of the predictions are very difficult to realize experimentally. For instance, CaH₆ should be synthesized at megabar pressures from Ca or CaH₂ in a hydrogen atmosphere at high temperatures to provide the solid-state reaction. The difficulties include the preparation of Ca which oxidizes easily, the fact that hot hydrogen readily breaks diamond anvils, and the solid-state reaction proceeds slowly. There are problems with electrical measurements, many materials are toxic, etc.

The appearance of H_2S on the long list of calculated hydrides [38, 39] was not too promising because of the low hydrogen content and the predicted T_c being lower than for other hydrides. On the other hand, this compound is available (while toxic), and the calculations were performed by a group which had already made successful predictions [44]. Experimental study [20], which can be seen below, showed a far more complicated picture than what was predicted by the theory [2].

2. Experimental results and discussions

The basic experimental techniques for the study include a method of low-temperature condensation of the gas and electrical measurements [20]. Gaseous H₂S was condensed in a cavity around anvils, and the liquid sample was clamped and then pressurized to megabar pressures at low temperatures to avoid dissociation, which was known to happen at room temperature and low pressures. The H₂S sample transformed into a metal at pressures above 100 GPa and superconductivity appeared, in reasonable agreement with the calculations [44]: T_c increased gradually with pressure (Fig. 2) and reached 60 K at 150 GPa. It is worthwhile to note that this superconducting transition temperature is likely the first correctly predicted by BCS theory [45] in the materials structural search. This was already a notable result-the highest $T_{\rm c}$ in a conventional superconductor. However, this successful story was 'spoiled' and hidden by a further increase in pressure; instead of the predicted drop in T_c , it dramatically increased to a very high value of 150 K (Fig. 2). Moreover,



Figure 2. (Color online.) Pressure dependence of T_c for annealed hydrogen sulphide (upper black symbols) and deuterium sulphide (lower symbols). Dashed straight lines indicate the pressure for transformation between phases R3m and Im3m.

 $T_{\rm c} = 203$ K was reached with the sample that was annealed at room temperature.

Further studies concentrated on the superconducting transitions with $T_{\rm c} \approx 200$ K. The superconductivity at these temperatures was confirmed: from the observed steep fall-off of R(T) curve with the measured zero resistance; by the shift of the superconductive steps to lower temperatures with a magnetic field, and detection of diamagnetism (Meissner effect). The magnetization measurements were performed in a SQUID magnetometer (in collaboration with Mainz Gutenberg University) with the aid of the newly designed DAC. Later on, the Meissner effect was observed in experiments on resonant nuclear scattering [46, 47]. The isotope effect—the shift of the superconductive transition to lower temperatures upon replacing hydride sulphide with deuterium sulphide-further supported the superconductivity and confirmed its formation mechanism as phononmediated conventional superconductivity (Fig. 2). Thus, experimentally, superconductivity with $T_c = 203$ K was firmly established.

The high value of T_c and its pressure dependence indicated that the superconductivity of this type related to a phase which had not been considered theoretically [45]. It was suggested in Refs [20, 48] that a higher hydride (H_4S or H_6S) can be responsible for the superconductivity with the higher $T_{\rm c}$: H₂S might disproportionate and transform into these higher hydrides plus elemental sulfur [48] (for elemental sulfur, $T_c < 25$ K, as measured separately in the same study [20]). This hypothesis was based on the hypervalency of sulfur: its ability to create compounds with a valency of more than 2, for instance, a stable SF₆ molecule. Disproportionation of H₂S was well-known, as elemental sulfur was evident in the X-ray measurements for P < 50 GPa and T < 300 K [44], but only the path of the dissociation to elemental sulfur and hydrogen was considered in all previous work [44, 45].

The suggestion that 200 K superconductivity is related to a higher hydride [48] was supported by theoretical calculations [49] which appeared at the same time as experimental study [48]. In this theoretical study, another system-a hydride with H₃S stoichiometry-was considered. It modelled the experiment of Strobel et al. [50] on the van der Waals compound $H_2S(H_2)_4$, which was studied up to 30 GPa. The calculations described Strobel's experiment and extended the structural search to higher pressures (up to 250 GPa). New phases of close structures, R3m and Im3m, were found, which differ only in the positions of hydrogen atoms. The temperature $T_{\rm c} \sim 200$ K estimated from the Allen–Dynes equations for the Im3m phase coincided with the value found in experiment [48]. This naturally suggested that the R3m and $Im\bar{3}m$ phases can relate to the experiment where H₃S might be in a mixture with sulfur, as a result of decomposition of the starting H₂S [48]. Soon, this path of decomposition to H₃S and elemental sulfur was confirmed in calculations [51-54] and experimentally using X-ray structural analysis [55].

The kinetics of the transformation from H_2S to H_3S is unusual. This is possibly a nearly continuous process proceeding through intermediate Magneli phases [56]. Each of the phases has its own T_c , and this explains a continuous increase in T_c upon loading at low temperatures (Fig. 3). This gradual, nearly barrierless transformation explains why the $H_2S \rightarrow H_3S + S$ reaction can occur in the solid state at low ambient temperatures in a very confined environment at megabar pressures, where solid-state transformations are expected to be sluggish.

The simple $\text{Im}\overline{3}\text{m}$ and R3m structures were carefully examined theoretically by different groups, and various methods [51, 57–78] (including anharmonism [79] and a number of other corrections [63]) confirmed that the $\text{Im}\overline{3}\text{m}$ phase indeed can be a conventional superconductor with



Figure 3. (Color online.) Pressure dependence of the critical temperature T_c . Blue symbols: T_c measured in an H₂S sample loaded and pressurized at low temperatures (100–250 K). Red symbols mark calculations [45–47]. Black symbols were measured from samples annealed at room temperature.

 $T_{\rm c} \sim 200$ K. The quantum effects — large zero-point motion, anharmonic corrections — are strong in H₃S [57, 58, 76] and have a significant influence on the superconductivity. The quantum effects also shift the pressure of the structural transition to around 150 GPa (Fig. 3).

Remarkably, superconductivity in H₃S can be viewed as superconductivity of metallic atomic hydrogen [49, 60, 64]. The mechanism of superconductivity is clearly the same as that predicted for metallic hydrogen: the combined effect of a high characteristic frequency due to the light mass of hydrogen and a strong coupling due to the lack of an electron core in hydrogen. The contribution to superconductivity from oscillating hydrogen atoms amounts to 92%, while the sulfur atoms play the role of a cage holding the hydrogen atoms [52, 64]. Critical temperature $T_{\rm c} \sim 200$ K falls in the range of values predicted for pure atomic hydrogen. The latest calculations for hydrogen give $T_c = 300$ K; they include corrections to anharmonicity. This effect can be very strong for some hydrides and is determined not only by the lightness of the hydrogen atoms but also by particular structures in the phonon spectra. In the case of atomic hydrogen, anharmonicity suppresses T_c by 6% [80].

3. Summary and perspectives

To summarize, 200 K superconductivity in sulfur hydrides can be considered as well established in light of the results of recent experimental and theoretical studies. The electrical measurements of 200 K superconductivity and the H_3S structure were confirmed and reproduced in other laboratories [55, 81].

It is also important to note that another high-temperature superconductor — covalent hydride H_3P — was soon found experimentally with $T_c = 100$ K [82]. The superconducting phase of this material is apparently metastable, as T_c drops on annealing. This is in amazing agreement with independent calculations that could not find a stable phase of H_3P with a high T_c [83] but revealed a metastable phase with a T_c that agrees with the experiments [84].

For further characterization of high-temperature superconductivity in H₃S, apparently the superconducting gap should be determined by tunneling, infrared, and electron Raman spectroscopy. Tunneling spectroscopy of conventional BCS superconductors is perhaps the most powerful tool to investigate the electron density of states near the Fermi level. It provides the most direct evidence of the mechanism responsible for superconductivity, and a clear picture of the underlying electron-phonon interactions [85]. It allows the superconductive gap, the spectra of electrons, phonons, magnons, and other excitations to be measured. The principle behind the tunneling spectroscopy is rather simple [13]. So far, it has been successfully used to pressures of about 3 GPa in large-volume hydrostatic pressure cells [86, 87]. It is very important to develop this technique for DAC. The basic arrangement of the tunneling measurements is very similar to the current techniques for electrical measurements [20]. The only, but important, addition needed is an insulation layer resided between an electrode and the sample. The layer (typically oxide) should be uniform and have the proper thickness to provide the tunneling current. While difficult, the preparation of this layer is well established. Typically, the Al₂O₃ layer is obtained by oxidation of an aluminum electrode. However, Al electrodes do not fit DAC. Oxidation of Ta or Nb electrode cells [86] seems to be a good solution for DAC — typically we use Ta electrodes, which have a good adhesion to a diamond surface. In spite of the likely simplicity of tunneling measurements, their interpretation run into obstacles.

Another powerful method for determining the electronphonon spectral density is infrared spectroscopy. Parameter $\alpha^2 F(\Omega)$ is central to conventional superconductivity theory. Detailed information on this function can be retrieved from frequency-dependent optical absorption and reflection experiments [85]. Here, $F(\Omega)$ is the density of vibrational modes with frequency Ω at the Fermi surface, and α is an electron-phonon coupling constant.

Raman scattering of light is an effective tool for the determination of the energy gap, as in conventional superconductors excitations across the energy gap are Ramanactive [88]. The electronic Raman spectrum has been observed, for instance, in V₃Si [89]. The Raman response, even in a 'clean' s-wave superconductor, has a distinct feature in the spectrum corresponding to the energy gap, even in the clean limit. Experimentally, the Raman effect is difficult to observe in metals. First, the Raman process is an intrinsically weak second-order process, much weaker than the dipole absorption responsible for optical conductivity. Second, electromagnetic radiation in conductors only penetrates a few thousand angströms, making the effective interaction volume small. Nevertheless, Raman scattering can be observed in metals and cuprate high-temperature superconductor, even under pressure in a diamond anvil cell [90].

Measurements in high magnetic fields (up to 100 T) give plenty of information on the basic properties of superconductors [20]: the superconducting gap, the coherence length ξ_{GL} , the London penetration depth λ_L , and the magnetic critical current density, which can be estimated by knowing the lower critical field H_{c1} and the upper critical field H_{c2} , along with their temperature dependences. Very high critical field H_{c2} of 70 T was estimated in the original measurements of electrical resistance performed in a moderate magnetic field of 7 T [20]. Further studies can be done in the fields on the order of 100 T. Various measurements can be done for a direct study of the Fermi surface: electrical transport, Shubnikov–de Haas and De Haas–van Alphen oscillations, and the Hall effect.

Is it possible to find superconductors with $T_{\rm c}$ higher than that in H_3S or even room-temperature T_c ? There are no reasons to think that H_3S is the highest- T_c material that will be found. Recently, other hydrides with $T_{\rm c}$ higher than that in H₃S have been predicted. Trends in superconductive properties in binary hydrides were discussed in Ref. [59]. In particular, CaH₆ is very interesting, as a T_c of ~ 230 K at 150 GPa [40] was predicted some time ago. Still, this has not been verified experimentally in spite of ongoing efforts by our and other groups. Recently, an even higher T_c of 260 K at 120 GPa was predicted in a similar compound YH_6 [41]. These compounds have interesting lattice structures which differ from H₃S structures: the atoms of Ca or Y have adopted a bcc structure with an H sodalite-like cage. While hydrogen form a strong covalent bonds with the sulfur atoms, no bonds were composed between the Ca (or Y) and H atoms. A weak 'pairing' covalent interaction was revealed between the H atoms that formed a square 'H4' lattice in CaH₆, and 'H6' hexagons in YH₆. The electron-phonon coupling parameters in both compounds are similar and very high: $\lambda = 2.69$ for CaH₆, and for cI14-YH₆ λ reaches 2.93. Hydrogen's contribution to superconductivity amounts to about 80%.

One of the well-known strategies to enhance superconductivity comprises carrier doping. In the case of H₃S, the position of the Fermi level can be shifted and adjusted to a van Hove singularity in the DOS (density of states) [57, 63, 66]. The calculations [91] showed that a partial substitution of sulfur atoms by phosphorus atoms increases the DOS and the coupling constant, and a T_c of 280 K can be reached. Possibly, the silicon or oxygen [66] substitution also increases T_c to 274 K. Another, but less likely, scenario of observing a higher T_c is to check if the pure H₃S compound has a higher T_c . So far, only a mixture of H₃S with elemental sulfur has been studied (it is formed as a result of dissociation of H₂S) [20].

What information can be gathered from the study of H_3S ? In contrast to the known high-temperature superconductors with a layered structure, H₃S has a highly symmetric threedimensional structure with a strong covalent bonding between sulfur and hydrogen atoms. The superconductivity in H₃S is basically well described by the BCS theory in the Migdal-Eliashberg formulation. The high-frequency phonons related to hydrogen apparently play a significant role in the superconductivity. However, the characteristic phonon frequency $\omega_{ln} \approx 1000 \text{ cm}^{-1}$ and electron–phonon coupling constant $\lambda = 1.67$ [70] are not particularly high. The case of H₃S clearly demonstrates that high-temperature superconductivity can be realized in materials with a modest content of hydrogen, and moderate values of the characteristic phonon frequencies and electron-phonon coupling constant. The high $T_{\rm c}$ seems to be determined by delicate details of the phonon and electron spectra. In this regard, it is instructive to compare H_3P with H_3S and understand why T_c in these similar compounds are so different. Oh et al. [58] found that their electronic structures are analogous; the maximum frequencies are also nearly the same (250 meV or 2000 cm^{-1}). The only difference lies in the distributions of phonons over the spectrum, and this circumstance results in very different values of ω_{ln} . In H₃S, the phonon spectrum is nearly ideally optimized [65], and as a outcome this leads to $\omega_{ln} = 136$ meV, in contrast to only 53 meV for H₃P [58].

The vagueness in predicting materials with high $T_{\rm c}$ from general ideas or empirical rules (see, for instance, Ref. [92]) indicates that the strategy for the search for new hightemperature superconductors should be changed—the search should be based on accurate evaluations of $T_{\rm c}$. Fortunately, the critical temperature and other parameters for conventional superconductors (such as H₃P) can be calculated and reliably estimated. Thus, the electron and phonon spectra can be determined from the structure which, in turn, can be obtained with the aid of available powerful methods for structure search. The structural search has been dramatically improved within recent years and appears to become more and more reliable. Calculations of the critical temperature can be included in the algorithm of the search [38, 93]. This might tremendously accelerate the discovery of potential superconductors with successive verification by experiment and its feedback. Moreover, a search for compounds with the highest $T_{\rm c}$ can reveal metastable states capable of being realized in experiments [82, 84].

Until the present time, only binary compounds have been theoretically studied. Ternary compounds will undoubtedly be considered, as the crystal structure search undergoes developing. The search will include existing materials, while new materials with high T_c can be designed [94] and then probably synthesized.

So far, we have considered covalent hydrides which are made metallic by the application of a high pressure. But the most interesting outcome, of course, consists in finding hightemperature superconductors at ambient pressure, which would be suitable for applications. There are many materials with high characteristic phonon frequencies and electronphonon coupling strengths [95]. They include not only hydrogen-containing materials but also carbon-based materials [96]: diamond (Debye frequency $\omega_D = 1860$ K), graphite, fullerenes, etc. [95]. They are intrinsically insulators, semiconductors, or semimetals but can be made metallic and superconducting by doping. A prominent example is the C_{60} compound doped with alkali atoms. These compounds are superconductors with $T_c = 33$ K at ambient pressure, and $T_{\rm c} = 38$ K is reached at high pressures for Cs₂RbC₆₀ [97]. At present, this is the highest value of T_c for organic superconductors. Critical temperature up to 18K has been observed for K-doped picene [96], and then T_c was increased to > 30 K in the C₃₀H₁₈ compound [98].

Another promising material for achieving high- T_c superconductivity is graphane (hydrogenated graphene) [99]. It is predicted to be a superconductor with $T_c \approx 90$ K at low accessible doping [100]. In the case of a multilayer system, T_c could be much higher: up to 160 K [101]. Graphene doped with Li will have T_c up to 18 K [102].

Carbon-based clathrates ¹ are another prospective superconductors [103]. The compound FC₃₄ is predicted to have T_c up to 77 K [104]. The T_c of sodalite-like NaC₆ is predicted to be above 100 K [105].

It should also be mentioned the possibility of high T_c in nanoclusters [13, 106]. We do not discuss here many other ideas on high-temperature superconductivity based on the BCS approach, for instance, 'gluing' electron pairs not with phonons but with excitons, etc. [11].

Ammonia is of special interest. Pure ammonia cannot be considered a potential superconductor. At high pressures, it does not turn into metal but instead transforms into an ionic solid which is an insulator to terapascal pressures [107]. A transformation to an ionic state of ammonia was confirmed experimentally [108]. However, ammonia, similar to fullerenes, can be effectively doped with alkali and other metals and will then have metallic conductivity (see review [109]). These ammonia-metal solutions or compounds have long attracted attention as possible high-temperature superconductors [110]. It is natural to revisit these compounds after finding high-temperature superconductivity in H₃S, as NH₃ can also be considered a hydrogen-rich material. Of course, the presence of hydrogen atoms in a metal is not a guarantee of emerging superconductivity; ammonia-metal solutions are very different from H₃S. In any case, ammonia-metal solutions are very interesting materials and have the potential for superconductivity, and definitely deserve careful study. In more detail, ammonia is a unique solvent that dissolves all the alkali metals, the alkaline-earth metals (Ca, Sr, and Ba), and the lanthanide metals (Eu and Yb). Thus, Li, Ca, Sr, Ba, Eu, and Y atoms form Li(NH₃)₄ and Ca(NH₃)₆ type compounds, whereas Na, Cs, and some other metals do not form compounds but solutions. The metals can be viewed also oppositely-as lattice-expanded metals in which the metal atoms are spatially separated by the diluent (i.e., dielectric ammonia).

¹ Compounds formed by the inclusion of guest molecules into the cage of host molecules.

The lithium-ammonia solution has received more attention than other ammonia-metal solutions. It forms a $Li(NH_3)_4$ compound [111]. The latter is the lightest metallic solid ($\rho = 0.57 \text{ g cm}^{-3}$), golden-bronze in color with the lowest melting point of any metal, equaling 88.8 K. It also possesses a modest electric conductivity of around 15,000 Ohm⁻¹ cm⁻¹ and a conduction-band electron number density of only 4×10^{21} cm⁻³ [110]. This is a compound which appears to occupy just the metallic side of the Mott (metal-insulator) transition. Application of pressure might shift the state to a better pronounced metal which will likely promote superconducting properties. However, calculations [111] showed a complex behavior under pressure loading, and it seems likely that this solution will be a poor metal under pressure. Nevertheless, it is not known whether the right structure was selected for the calculations. An experimental check should be done.

A saturated solution of Na in NH₃ is exceedingly interesting [110], because Ogg [112] observed anomalously high conductivity in this compound. However, possible superconductivity with the critical temperature of 230 K was not reliably reproduced in his experiments (7 times in about 200 experimental runs) [110]. Succeeding work did not support superconductivity, but still the picture was not clear and experiments searching for the superconducting transition in Na:NH₃ have been repeated from time to time. Probably, the most comprehensive experiments were carried out by Dmitrenko and Shchetkin [113]. They studied the temperature and time dependences of the resistance R of metalammonia solutions with various sodium concentrations (1-12 at.%) over a wide temperature interval T=20-240 K. The authors concluded that this system may be superconducting. Another explanation for the high conductivity was claimed in Ref. [114]. Was Ogg [112] right in terms of the experimental observation of high-temperature superconductivity in quenched Na:NH₃ solutions? Edwards [110] believes that this key issue has not yet been finally settled.

4. Conclusion

It seems likely that the discovery of high T_c in H₃S [20] will revitalize interest in conventional superconductors and new materials will sooner or later be found. One recent example is the report on possible superconductivity with $T_c = 5$ K in palladium hydride, and 60 K in palladium deuteride at ambient pressure [115]. This is a record-high T_c for conventional superconductors at ambient pressures. Hopefully, the materials of this type will be further characterized and checked in different laboratories.

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