Magnesium compounds as future high temperature superconductors

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Abstract. Previously proposed method for calculating the superconducting transition temperature (Tc) of the different substances was used to predict Tc of magnesium compounds. Theoretical calculations show the good agreement with experimental results for MgB2, the only magnesium compound with experimentally proved Tc = 39 K (theoretical value is 40.5 K). The performed computations for binary compounds Mg2X (X: Ge, Sn, Pb) reveal the high potential of magnesium compounds as high-temperature conductors at normal pressure, with predicted superconducting transition temperature up to 70 K.

1. Introduction
In 1911, the Dutch physicist Heike Kamerling-Onnes discovered the phenomenon of superconductivity [1, 2]. More than 100 years later, superconductivity at helium and nitrogen temperatures was found in many metals and alloys, in intermetallic compounds, in ceramics [3], in fullerene and graphene, as well as in hydrides (H2S, LaH10) at ultrahigh pressure [4].

Inaugurating a new era of high-temperature superconductivity, lanthanum and yttrium ceramics, display critical superconducting temperature Tc > 60 K [3]. In [5] we highlighted the common to all above-mentioned substances properties that determine the attainable Tc level: the heats of formation of both elements and compounds; the energy of formation of defects in the substances; the melting temperature; the Debye frequency; the harmonic oscillator energy, considering the lattice atoms as harmonic oscillators. The paper considers the potential of magnesium compounds as high-temperature superconductors on the basis of physicochemical analysis of phase diagrams.

2. Theoretical aspects
In [5] we proposed the equation for calculating Tc:

$$T_c = \frac{h \nu_D}{k} \exp \left( \frac{-H_{V,1}}{n_{1,2,3} \cdot \varepsilon_{rel}} \right),$$

where h - is the Planck constant, νD - is the Debye frequency (referred to 0 K), k - is the Boltzmann constant, n1,2,3 - is for one-, two-, and three-dimensional oscillator, HV,1 - is the energy of the formation of defects in them. One can calculate the formation energy of mono-vacancies as TmSm for the solid phase, as well as using the formula: $H_{V,1} = \left(2G_0V_0 \cdot \varepsilon_{rel} \right)^{1/2}$, where G0V0 is the elastic shear energy at 0
K, and $\varepsilon_{rel}$ is the average relaxed energy of the oscillator, that is equal to the heat of formation of the substance from the liquid phase. Moreover, the value of $H_{v,1}$ (determined by quenching a solid from $T$, close to $T_m$ - the melting temperature) includes practically all the co-occurring defects (change in bond lengths, angle between them, i.e. their energy).

3. Calculation results

To start with consider magnesium diboride MgB$_2$, nowadays commercially used superconductor with $T_c = 39$ K [6]. Pure Mg has a low $T_c \approx 0.05$ K (at normal pressure), $H_v = 50.000$ kJ/mol, $\varepsilon = 8.954$ kJ/mol; $\theta^0_B$, the characteristic temperatures, determined from the elastic constants and the calorific value are 386 and 406 K, respectively, so we have $T_{c1} = 1.45$ and $T_{c2} = 1.53$ K. The calculated heat of formation of MgB$_2$ is $\varepsilon = 22.931$ kJ/mol. Assuming that Mg precipitations during the low-temperature decomposition of this compound will determine superconductivity, we calculate $T_c$ taking into account the fact that $H_{v,Mg} = 50.000$ kJ/mol, $\theta^0_B = 386$ K (for boron, $H_v = 95.000$ kJ/mol). Thus, for MgB$_2$ we have $T_c = 43.6$ K, but if we use the value $H_v = 54.056$ kJ/g-at, $T_c$ would be 36.5 K. The average value is $40.05$ K, which is close to the experimental (39 K). Note that the Mg-B diagram at normal pressure has not yet constructed. A certain temperature of the equilibrium is 1050°C (1323 K), and the powders of MgB$_2$ samples are sintered at 973 K.

One should pay attention to magnesium compounds of the Mg$_2$X type, where X – Ge, Sn, Pb, La, as well as others, for example, Mg$_2$Sb and Mg$_2$Bi$_2$. Preliminary calculations show the possibility of reaching $T_c > 50$ K for these compounds. These compounds can be prepared both by the powder and by the melting method. The major liability of the above magnesium compounds is that they are hygroscopic when aged in the air under normal conditions.

The Mg$_2$Ge compound ($e/a = 2.7$, the same as for MgB$_2$) has $T_m = 1388$ K (see Figure 1), and the high heat of phase formation (heat of fusion) or the maximum relaxed energy of a one-dimensional oscillator $\varepsilon_{rel}$ (for the solid phase). Taking into account that Mg and Ge have the similar defect formation energies ($H_v$, respectively, 50.000 and 55.000 kJ/mol, $\varepsilon_{rel} = 28.570$ kJ/mol, at $T = 386$ K) we have $T_c = 67$ K, i.e. no worse than that of pnictides. Of course, in the presence of covalent bonds, the result can be lower (\sim 12 K), however, when choosing the appropriate “doping” additives, good results can be obtained (for example, Ba or oxides can break covalent bonds).

Mg$_2$Sn phase holds much promise having $T_m = 1051$ K (Figure 2), $\varepsilon_{calc} = 19.494$ kJ/mol. Taking into account the excess of Mg in this compound, calculations give $T_c = 30.9$ K (in the case of covalent bonds, the “dopants” are necessary, since $T_c = 2.3$ K would be). An excess of tin ($\theta^0_B = 201$ K) with $H_{v,Sn} = 50.000$ kJ/mol gives $T_c = 15.3$ K, but if we apply the concept of a two-dimensional oscillator to Sn (that is typical for free tin), we obtain $T_c = 55.5$ K without “doping additives” that can enhance this value. This system, with affordable and inexpensive metals, also deserves development.

The Mg-Pb system is distinguished by one Mg$_2$Pb compound with a low melting temperature, $T_m = 823$ K (Figure 3), $H_{v,Pb} = 48.000$ kJ/mol; $H_{v,Mg} = 50.000$ kJ/mol; then $T_{c,Mg} = 6.15$ K and $T_{c,Pb} = 2$ K, however, in the case of excess Pb (data for free Pb calculated from a three-dimensional oscillator), we have $T_c = 29$ K, i.e. just below $T_c = 30$ K for high-temperature superconductors (HTSC). A calculation with the experimental value $\varepsilon = 13.395$ kJ/mol for this phase and $\theta^0_B = 111$ K gives $T_c = 33.6$ K.
Figure 1. Ge-Mg phase diagram [7].

Figure 2. Mg-Sn phase diagram [7].

Figure 3. Mg-Pb phase diagram. [7].
Before addressing the compound Mg₃Sb₂ (Figure 4), we calculate $T_c$ for antimony. Sb has $H_v = 40.000$ kJ/mol, its $\varepsilon_{rel} = 19.842$ kJ/mol, $\theta_{D,\text{Sb}}^0 = 200$ K, then, given the fact that antimony melts as Sb₂, we have $T_c = 3.55$ K. The metallic properties of antimony are more pronounced (i.e. electrical conductivity, thermal conductivity), and under normal pressure conditions, it is a superconductor at $T_c = 2.6 - 2.7$ K; and at $P > 85$ kbar, antimony has $T_c = 3.6$ K [1]. For the Mg₃Sb₂ compound, $T_m = 1501$ K. Low-temperature decay from the magnesium side (902 K) and from antimony side (852 K), $\varepsilon_{\text{exp}} = 30.558$ kJ/mol. The calculations of the temperature of the superconducting transition give for Mg excess: $T_c = 75.2$ K, and from the antimony side $T_c = 54$ K; this is the high result (for $\varepsilon_{\text{exp}} = 30.558$ kJ/mol), however, it can be less if the compound (and this is the case) will have covalent bonds, then for the two cases we have $T_{c,Mg} = 14.6$ K and $T_{c,Sb} = 14.6$ K, i.e. the same result, but high enough to investigate this system and to make use of doping.

![Figure 4. Mg-Sb phase diagram [7].](image)

Similar calculations one can make for the Mg₃Bi₂ and other phases of the Mg-Bi system, where two eutectics are observed, widely different in temperature. It is also necessary to study the Mg₃La phase, the other phase based on the elements lying behind the Zintl line, as is true for the MgB₂ compound ($T_c = 39$ K). Hexagonal lattices can be unstable to vibrations in the basal plane (see $c_{66}$ constant). If the structures listed above are stable to low temperatures, then it is difficult to expect that relaxation vibrations will arise in such the structures at low temperatures (the promising Mg₃Si phase). Mg₃Si structure is similar to that of fluor spar (4 AB₂ molecules in a cube cell), is not hexagonal (like MgB₂, P6mm). In any case, these structures could be surface-unstable, and doping can make them volume-unstable. And low $H_v / \varepsilon_{rel}$ ratio indicates the high concentration of defects, but the destruction of long-range order in structures with covalent metal bonds hindered. Mg₃Sb₂ intermetallic compound is of particular interest, for it undergoes the polymorphic $\beta \rightarrow \alpha$ transformation, while in the other intermetallic compounds order-disorder transitions are second-order transformations.

4. Conclusions

On the basis of physicochemical analysis of binary Mg-X (X: B, Ge, Sn, Pb, Sb) phase diagrams and the thermodynamic properties of the constituents the superconducting transition temperatures were calculated for MgB₂ ($T_c = 40.5$, the experimental $T_c = 39$ K), Mg₂Ge ($T_c = 67$ K), Mg₂Sn ($T_c = 55.5$ K),
Mg$_2$Pb ($T_c = 29$ K), and Mg$_3$Sb$_2$ ($54 < T_c < 75$). Thus, magnesium compounds of the Mg$_2$X type (X – Ge, Sn, Sb) can serve as the basis for the development of a new-generation HTSC with $T_c \sim 60 - 70$ K, i.e. no lower than that of compounds based on FeAs, and without ultrahigh pressures application.

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