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This article is dedicated to the memory of Chief Warrant Officer Gazinur Z. Kiiamov (1954–2024), Head of the Fuel and Lubricants Service Unit at the Plesetsk Cosmodrome.

On the efficiency of Mg/Nb diboride solid solution in enhancing the thermal stability of MgB_2 superconductor

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Abstract

A comparative analysis of the thermal stability of $Mg\,/\,Nb$ diboride solid solution and pure MgB_2 was carried out. The specific heat capacity of these materials below the critical temperature of MgB_2, which is an essential characteristic for assessing their thermal stability, was evaluated. Based on the *ab initio* calculations of the phonon density of states for both compounds, it was demonstrated that $MgNbB_4$ is characterized by a higher phonon density of states in the frequency range of 5–7.5 THz compared with MgB_2. $MgNbB_4$ was also found to exhibit a higher heat absorbing capacity at low temperatures. The specific heat capacity of $MgNbB_4$ at low temperatures exceeds that of MgB_2 by 50 %, thus indicating its better thermal stability. The potential of $MgNbB_4$ solid solution for practical application in superconducting wires made of MgB_2 was outlined.

Keywords: superconductivity, magnesium diboride, phonon

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ОРИГИНАЛЬНАЯ СТАТЬЯ
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Настоящая статья посвящена памяти начальника подразделения службы горюче-смазочных материалов космодрома Плесецк — старшего прапорщика Газинура Загировича Киямова (1954–2024).

Об эффективности твердого раствора диборида Mg/Nb в обеспечении термической стабильности сверхпроводника MgB_2

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Аннотация

Представлен сравнительный анализ термической стабильности твёрдого раствора диборида магния-ниобия (Mg/Nb) и типичного MgB_2. Исследована удельная теплоёмкость этих материалов ниже критической температуры MgB_2, которая является важным параметром при оценке их термической стабильности в сверхпроводящем режиме. На основе *ab initio* расчётов колебательных свойств и теплоёмкости для обоих соединений показано, что $MgNbB_4$ имеет более высокую плотность фононных состояний в диапазоне частот 5–7.5 ТГц по сравнению с MgB_2, что свидетельствует о его повышенной теплоёмкости при низких температурах. Установлено, что при низких температурах удельная теплоёмкость $MgNbB_4$ превышает таковую для чистого MgB_2 на 50 %, благодаря чему твёрдый раствор проявляет более высокую термическую стабильность. Отмечается высокий потенциал твёрдого раствора $MgNbB_4$ для практического применения, например, в составе сверхпроводящих проводников на базе MgB_2.

Ключевые слова: сверхпроводимость, диборид магния, фонон

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Introduction

The discovery of superconductivity in magnesium diboride (MgB_2) marked a major breakthrough in condensed matter physics [1]. Since its identification as a superconductor in 2001 [2], this simple binary compound has attracted much attention due to its high critical temperature (T_c=39 K) making it one of the most promising candidates for practical application in superconducting technology [3].

Searching for materials with tailored properties is a fundamental task of modern solid-state physics, which is driven by the need to deepen our understanding of matter. This also involves the modification and enhancement of existing materials.

The performance of superconductors is largely determined by the critical temperature of phase transition, i.e., superconductivity is temperature-dependent. Superconductors requiring higher temperatures are more practical. Therefore, most research efforts in superconductivity focus on finding materials that become superconductive at increasingly higher temperatures. However, while the pursuit of higher transition temperatures remains a central objective, and a challenge as well, it is important to emphasize that the practical applicability of superconductors is not exclusively defined by this property. Instead, researchers have gradually become more active in developing materials that are both technologically viable and easily accessible, ensuring that they possess a combination of properties optimal for real-world applications. These initiatives have arisen from the awareness that, for many practical purposes, a modest increase in the transition temperature may not justify sacrificing other beneficial characteristics, such as thermal stability, mechanical robustness, ease of fabrication, or accessibility. A reduction in one property, such as the transition temperature, can be acceptable and reasonable if it leads to a significant improvement in other critical characteristics. Hence, a more complex perspective is needed to comprehensively evaluate superconductors in terms of their potential use. It would bring substantial progress in the field, advancing the frontiers of superconducting technology. Prioritizing the utility and practical viability of superconducting materials over striving for higher transition temperatures opens the way for transformative advancements in materials science and the application of superconductors in industry.

When exposed to varying temperatures in the superconducting regime, Mg/Nb diboride solid solutions exhibit high thermal stability, which explains their efficiency as superconducting candidates. The thermal stability of a material is defined by its specific heat capacity, which is the energy demand of a substance as the temperature rises. Materials with a higher specific heat capacity absorb more thermal energy with minimal temperature fluctuations under the impact of heat and are thus more resistant to thermal variations. Ensuring the thermal stability of superconductors is an important aspect of their successful application. The temperature should be maintained below its critical point value. Otherwise, a superconductor may lose its superconducting properties: temperature fluctuations can degrade the performance of superconductors or even destroy the superconducting state. A higher specific heat capacity below the critical temperature enhances the thermal inertia of a superconductor. This effect can be interpreted as an expansion of the thermal reservoir, providing an additional mechanism to improve the thermal stability of a superconductor.

Most superconductors are non-magnetic compounds. Their specific heat capacity at low temperatures is affected by atomic oscillations, commonly described in terms of phonon quasi-particles. The dependence of the specific heat capacity on temperature can be manipulated by changing the phonon density of states.

When phonon frequencies shift to lower values, the specific heat capacity of a superconductor at lower temperatures increases. It absorbs more heat before the critical point is reached at which it stops being superconducting. As a result, the superconductor becomes more thermally stable, and the risk of accidental quench (a sudden loss of superconductivity) is reduced because it can handle more unexpected heat loads without failing.

$MgNbB_4$ is considered here to be a promising candidate for developing a MgB_2 analog with higher specific heat values below the critical temperature. Both compounds have a similar crystal structure with nearly identical lattice symmetry and close lattice constant values [4].

MgB_2 and NbB_2 have different critical temperature values, and the exact critical temperature of $MgNbB_4$ solid solution is unknown. However, even if the critical temperature of $MgNbB_4$ solid solution is extremely low, it can still be used as an extra layer on the MgB_2 tape or in any other configuration, such as in a checkerboard-type pattern of long bars. Since these compounds have nearly identical lattice constants, creating such composites seems feasible. The structural similarities of $MgNbB_4$ and MgB_2 also suggest that high-quality interfaces can be achieved on the surface of that compound.

The purpose of this study is to explore the thermal stability of Mg/Nb diboride solid solution and MgB_2 and identify the potential for practical application of $MgNbB_4$ solid solution, such as in superconducting wires.

1. Methods

The vibrational properties of MgB_2 and $MgNbB_4$ were determined by *ab initio* calculations of the phonon density of states (DOS). The density functional theory calculations were performed using the *Vienna* ab initio *simulation package* (VASP) within the *MedeA* software [5]. The phonon DOS was analyzed through a *direct approach* of harmonic approximation. The *direct approach* to studying the lattice dynamics was based on the *ab initio* evaluation of the forces acting on all atoms through a set of finite displacements of a few atoms within an otherwise perfect crystal [6].

The exchange and correlation effects were described by the generalized gradient approximation as parameterized by Perdew, Burke, and Ernzerhof. The Kohn–Sham equations were solved using projector-augmented wave potentials and wave functions. The plane-wave cutoff was set to 500 eV. The energy tolerance for the self-consistency loop was equal to 10^{-7} eV. The Brillouin zone was sampled on Monkhorst-Pack grids with 0.25 points per Å. Equilibrium geometry was obtained after several rounds of full structural relaxation including atomic positions, cell shape, and cell volume.

2. Results and Discussion

Fig. 1. shows the calculated phonon DOS for MgB_2 and $MgNbB_4$. Both compounds exhibit a complex structure with multiple peaks. In terms of partial atomic contributions, the PDOS can be divided into two distinct regions. Low-energy oscillations (up to 10 THz) are induced by the Mg and Nb modes in both pure MgB_2 and $MgNbB_4$. In $MgNbB_4$, the first phonon DOS peak (up to 7.5 THz) originates from Nb ions, while the next peaks (from 7.5 to 10 THz) correspond entirely to the Mg modes. High-energy oscillations (from 10 to 27 THz) for both compounds consist only of the B modes. This study is focused on the low-temperature thermal behavior of MgB_2 and $MgNbB_4$, so the changes in the high-frequency range are not relevant to us.

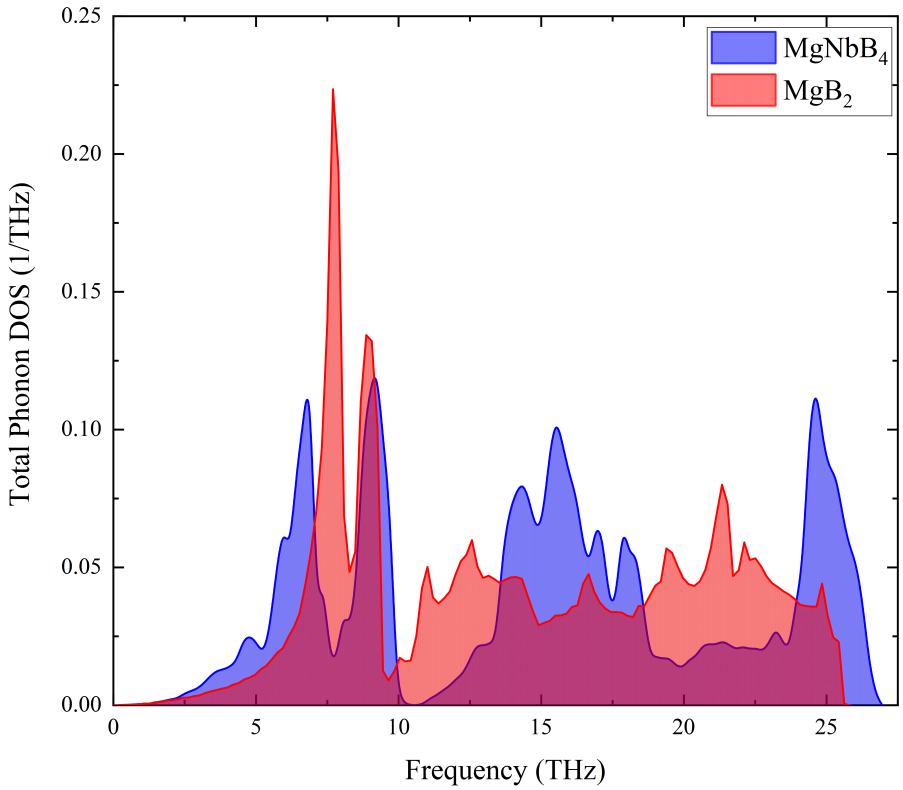

Fig. 1. Calculated phonon density of states as a function of frequency. Red color – pure MgB_2, blue color – $MgNbB_4$

A side-by-side comparison of the low-frequency regions for MgB_2 and $MgNbB_4$ reveals that the first peak in the phonon DOS of $MgNbB_4$ occurs at frequencies lower than those of MgB_2. This observation suggests that $MgNbB_4$ is likely to have a higher heat absorbing capacity at low temperatures compared with MgB_2.

To test this hypothesis, the lattice term for the specific heat of MgB_2 and $MgNbB_4$ was determined using the calculated phonon DOS, as expressed in the following equation:

$$C = Dk_B \int g(\omega) \left(\frac{\hbar\omega}{2k_BT}\right)^2 \frac{exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left(exp\left(\frac{\hbar\omega}{k_BT}\right) - 1\right)^2} d\omega,$$

where D stands for the degrees of freedom in a unit cell, $g(\omega)$ is the phonon DOS. See [7] for more details. The calculated lattice specific heat C_v^L for MgB_2 and $MgNbB_4$ is given in Fig. 2.

Fig. 2 illustrates that, in the low-temperature range, the lattice contribution to specific heat follows a cubic trend in temperature, as predicted by the Debye theory, for both MgB_2 and $MgNbB_4$.

Due to the higher phonon DOS of the $MgNbB_4$ in the low-frequency range (Fig. 1), its specific heat capacity at low temperatures is higher than that of pure MgB_2 (Fig. 2, blue region). This trend continues up to 100 K, where the two curves intersect. With further increase in temperature, the heat capacity of pure MgB_2 exceeds that of $MgNbB_4$. The integration of $C_v^L(T)$ from 0 to 39 K (the critical temperature of MgB_2) yields the heat values of

$\Delta Q^L_{MgB_2} = 3.2\,J/mol$ and $\Delta Q^L_{MgNbB_4} = 4.8\,J/mol$ for MgB_2 and $MgNbB_4$, respectively. Taking in account the molar weights and densities of both compounds, the heat values ΔQ can also be expressed per volume unit (the density of $MgNbB_4$ was estimated as an arithmetic mean of MgB_2 and NbB_2 densities). Thus, $\Delta Q^L_{MgB_2} = 0.18\,J/cm^3$ and $\Delta Q^L_{MgNbB_4} = 0.27\,J/cm^3$ for MgB_2 and $MgNbB_4$, respectively.

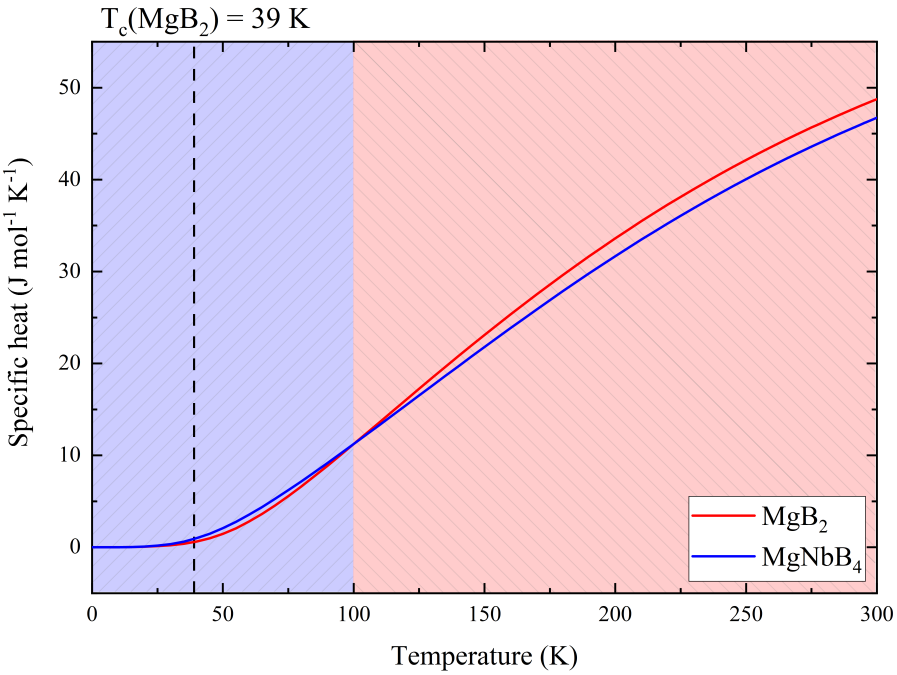

Fig. 2. Temperature dependencies of the calculated lattice specific heats $C^L_v(T)$ for MgB_2 and $MgNbB_4$

Therefore, the ability of $MgNbB_4$ to function as a heat reservoir before reaching its superconducting phase transition temperature is 50 % greater compared to MgB_2 in equal volume.

Conclusions

A comparative analysis of the thermal properties exhibited by $MgNbB_4$ and MgB_2 was performed. The results reveal that $MgNbB_4$ is characterized by a significantly higher phonon DOS than MgB_2 in the frequency range of 0–7.5 THz, which corresponds to the temperatures of 0–360 K.

$MgNbB_4$ solid solution has a stronger potential for use in superconducting wires because of how its crystal lattices vibrate compared with MgB_2. These differences in the vibrational properties affect their specific heat capacity at lower temperatures. The lattice contribution into the specific heat capacity is higher in $MgNbB_4$ than in MgB_2 throughout the entire superconducting temperature range of MgB_2 (0–39 K) and then up to 100 K. It means that $MgNbB_4$ can absorb more heat before reaching the critical temperature where superconductivity is lost. The thermal reservoir capacity of this compound is about 50 % greater than that of MgB_2 in the same volume: $\Delta Q^L_{MgNbB_4} = 0.27\,J/cm^3$ and $\Delta Q^L_{MgB_2} = 0.18\,J/cm^3$, respectively.

Therefore, $MgNbB_4$ solid solution may be successfully applied to improve the thermal stability of MgB_2 by synthesizing them into composites of various geometry, multilayered hetero-interfaces of these compounds. The qualitative and quantitative similarities between the crystal structures of both compounds make it feasible to produce such solids [4]. One must consider that the superconducting properties of Mg/Nb diboride solid solutions are still not completely understood. In this study, $MgNdB_4$ was assumed to be a non-superconducting material, and, if it does exhibit superconductivity, its potential for practical application is even higher.

Conflicts of Interest. The authors declare no conflicts of interest.

Конфликт интересов. Авторы заявляют об отсутствии конфликта интересов.

References

1. Bianconi A., Di Castro D., Agrestini S., Campi G., Saini N.L., Saccone A., De Negri S., Giovannini M. A superconductor made by a metal heterostructure at the atomic limit tuned at the 'shape resonance': MgB_2. *J. Phys.: Condens. Matter*, 2001, vol. 13, no. 33, art. 7383. https://doi.org/10.1088/0953-8984/13/33/318.

2. Buzea C., Yamashita T. Review of the superconducting properties of MgB_2. *Supercond. Sci. Technol.*, 2001, vol. 14, no. 11, art. R115. https://doi.org/10.1088/0953-2048/14/11/201.

3. de Castro Sene F.C. Review on the state-of-the-art and challenges in the MgB_2 component manufacturing for superconducting applications. *Superconductivity*, 2024, vol. 9, art. 100083. https://doi.org/10.1016/j.supcon.2023.100083.

4. Choi H.J., Roundy D., Sun H., Cohen M.L., Louie S.G. The origin of the anomalous superconducting properties of MgB_2. *Nature*, 2002, vol. 418, no. 6899, pp. 758–760. https://doi.org/10.1038/nature00898.

5. Wimmer E., Christensen M., Eyert V., Wolf W., Reith D., Rozanska X., Freeman C., Saxe P. Computational materials engineering: Recent applications of VASP in the MedeA software environment. *J. Korean Ceram. Soc.*, 2016, vol. 53, no. 3, pp. 263–272. https://doi.org/10.4191/kcers.2016.53.3.263.

6. Parlinski K., Li Z.Q., Kawazoe Y. First-principles determination of the soft mode in cubic ZrO_2. *Phys. Rev. Lett.*, 1997, vol. 78, no. 21, pp. 4063–4066. https://doi.org/10.1103/PhysRevLett.78.4063.

7. Kiiamov A.G., Lysogorskiy Y.V., Vagizov F.G., Tagirov L.R., Tayurskii D.A., Seidov Z., Krug Von Nidda H.-A., Tsurkan V., Croitori D., Günther A., Mayr F., Loidl A. Vibrational properties and magnetic specific heat of the covalent chain antiferromagnet. *Phys. Rev. B*, 2018, vol. 98, no. 21, art. 214411. https://doi.org/10.1103/PhysRevB.98.214411.

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