Pis'ma v ZhETF, vol. 109, iss. 9, pp. 627 – 628

Electron-phonon interaction, phonon and electronic structures of layered electride Ca_2N

B. N. Mavrin[+], *M. E. Perminova*[+], *Yu. E. Lozovik*[+*×1)]

[+]*Institute of Spectroscopy of Russian Academy of Sciences, 142190 Troitsk, Moscow, Russia*

[*]*Moscow Institute of Electronics and Mathematics, National Research University Higher School of Economics, 101000 Moscow, Russia*

[×]*Dukhov Research Institute of Automatics (VNIIA), 127055 Moscow, Russia*

Submitted 27 March 2019
Resubmitted 27 March 2019
Accepted 27 March 2019

DOI: 10.1134/S0370274X1909011X

The phonon and electronic properties, the Eliashberg function and the temperature dependence of resistance of electride Ca_2N are investigated by the DFT-LDA (density functional theory in local density approximation) plane-wave method. The phonon dispersion, the partial phonon density of states and the atomic eigenvectors of zero-center phonons are studied. The electronic band dispersion and partial density of states conclude that Ca_2N is a metal and the Ca 3p, 4s and N 2p orbitals are hybridized. For the analysis of an electron-phonon interaction and its contribution of the Eliashberg function to resistance was calculated and a temperature dependence of resistance due to electron-phonon interaction was found.

There is considerable interest in layered electrides in bulk and monolayer forms in which *playing anionic role* electrons form two-dimensional planes separated from positively charged layers of ions [1–6]. In view of their promising properties such as high electrical conductivity, low work function, and significant catalytic activity in their ideal form, electrides are perspective for use in next-generation electronics.

Sub-nitride Ca_2N belongs to this new class of layered-structure electrides with the two-dimensional delocalized layers of electrons [7, 8]. The rhombohedral unit cell of Ca_2N contains more electrons than it is expected from the simple electron counting rules. It is supposed that excess electrons are localized between positively charged layers $[Ca_2N]^+$. The physical properties of Ca_2N were studied by photoelectron spectroscopy [7, 9], optical reflectance spectroscopy [7], electrical conductivity [7, 10], by study of magnetic susceptibility [10] and magnetoresistance [7]. It was found that single crystal Ca_2N exhibits metallic transport with resistivity, which is smaller than that of pure Ca metal [7]. The temperature dependence of resistivity indicated that the electron-electron interaction could be much stronger than the electron-phonon interaction even in the high-temperature region [7].

In this Letter we calculate the Eliashberg function of Ca_2N from first principles (DFT) to estimate the electron-phonon interaction (EPI) and its contribution to resistance as well as a temperature dependence of resistance caused EPI.

We start our calculations from the study the phonon and electronic properties of the Ca_2N crystal in order to compare with calculations [11, 12] of these properties in the isolated layer Ca_2N and to obtain the density of phonon states $F(\omega)$ that is necessary to compute EPI. Besides, in distinct from previous calculations [11, 12], we had to use the relativistic pseudopotentials [13, 14] in first-principles calculations of EPI. The frequencies of phonon branches have been calculated within density perturbation theory [15]. There was no an energy gap between acoustic and optic branches in the phonon dispersion. If the main contribution of the N atoms in phonon density $F(\omega)$ locates above $285\,\mathrm{cm}^{-1}$, the Ca atom gives a contribution at lower frequencies except for acoustic modes in which a participation of both atoms is noticeable. We have found, the electron density of states at the Fermi level is finite, that is, Ca_2N is a metal.

The role of different phonon branches in electron-phonon interactions can be characterized by the spectral Eliashberg function $\alpha^2F(\omega)$ [16, 17] where α^2 is the squared effective EPI. The calculations of $\alpha^2F(\omega)$ were performed by the method [18]. The main peaks in phonon density $F(\omega)$ are seen also in function $\alpha^2F(\omega)$, confirming a contribution of almost all phonons to the Eliashberg function in Ca_2N. We calculate the resistance only due to electron-phonon interactions. In this

1) e-mail: lozovik@isan.troitsk.ru

case the temperature dependence of electrical resistivity can be calculated in the lowest-order variational approximation [18] using the calculated function $\alpha^2 F(\omega)$, density of the electronic states at the Fermi level and average square of the Fermi velocity for electrons. The calculated resistance ρ of Ca_2N turned out to be highly anisotropic, and it is visibly higher along the axis z. This result is consistent with experimental estimates. The small value of ρ_x is in agreement with idea of presence of a two-dimensional layer of electrons between positively charged layers $[Ca_2N]^+$ [7, 8] and with our calculated electronic structure, from which it follows that Ca_2N should have a metallic character along the plane of the layers.

In summary, we have presented a first-principles study of phonon and electronic structures and resistance of electride Ca_2N at the LDA level taking into account semi-core electrons for the Ca atom and using the plane-wave pseudopotential method. The phonon properties such as the phonon dispersion, the partial phonon density of states and the eigenvectors of zone-center optic modes are investigated. All phonons make a significant contribution to electron-phonon interactions in Ca_2N. The calculated resistance of Ca_2N turned out to be highly anisotropic, and it is visibly lower along the plane of the layers.

We would like to thank Dr. T. A. Ivanova for assistance.

The use of facilities of the Joint Supercomputer Center of Russian Academy of Sciences is greatly appreciated. The work was supported by Russian Foundation of Basic Research grants # 17-02-01134 and 18-52-00002.

Yu. E. Lozovik was supported by the Program of Basic Research of Higher School of Economics.

Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364019090029

1. P. Cudazzo and M. Gatti, Phys. Rev. B **96**, 125131 (2017).
2. D. L. Druffel, K. L. Kuntz, A. H. Woomer, F. M. Alcorn, J. Hu, C. L. Donley, and S. C. Warren, J. Am. Chem. Soc. **138**(49), 16089 (2016).
3. M. Hiraishi, K. M. Kojima, I. Yamauchi, H. Okabe, S. Takeshita, A. Koda, R. Kadono, X. Zhang, S. Matsuishi, H. Hosono, K. Hirata, S. Otani, and N. Ohashi, Phys. Rev. B **98**, 041104(R) (2018).
4. L. Zhang, W. Yu, J.-Y. Ou, Q. Wang, X. Cai, B. Wang, X. Li, R. Zhao, and Y. Liu, Phys. Rev. B **98**, 075434 (2018).
5. Ch. Park, S. W. Kim, and M. Yoon, Phys. Rev. Lett. **120**, 026401 (2018).
6. Y. Zhang, H. Wang, Y. Wang, L. Zhang, and Y. Ma, Phys. Rev. X **7**, 019903 (2017).
7. K. Lee, S. W. Kim, Y. Toda, S. Matsuishi, and H. Hosono, Nature **494**, 336 (2013).
8. A. Walsh and D. O. Scanlon, J. Mater. Chem. C **1**, 3525 (2013).
9. U. Steinbrenner, P. Adler, W. Holle, and A. Simon, J. Phys. Chem. Solids **59**, 1527 (1998).
10. D. H. Gregory, A. Bowman, C. F. Baker, and D. P. Weston, J. Mater. Chem. **10**, 1635 (2000).
11. C. M. Fang, G. A. de Wijs, R. A. Groot, M. T. Hintzen, and G. de With, Chem. Mater. **12**, 1847 (2000).
12. S. Guan, S. A. Yang, L. Zhu, J. Hu, and Y. Yao, arXiv: 1502.02321.
13. C. Hartwigsen, S. Godecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).
14. H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
15. S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
16. G. M. Eliashberg, Sov. Phys. JETP **11**, 696 (1960).
17. P. B. Allen, Phys. Rev. B **17**, 3725 (1978).
18. S. Y. Savrasov and D. Y. Savrasov, Phys. Rev. B **54**, 16487 (1996).