FIRST PRINCIPLE STUDY OF VIBRATIONAL AND THERMODYNAMIC PROPERTIES OF SUPERCONDUCTING $ZnNNi_3$

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ABSTRACT

An investigation on the phonon and thermodynamic properties of superconducting $ZnNNi_3$ has been conducted using the norm-conserving pseudopotential method, which is based on the first-principle density functional perturbation theory (DFPT) with local density approximation (LDA). Our calculated results suggested that the $ZnNNi_3$ is dynamically unstable, which is the characteristic of the phase changing material. The Debye temperature and the longitudinal and transverse sound velocities have been calculated. To the best of our knowledge there are no available data in literature for comparison. So, our calculated results can be seen as a prediction for future investigations.

Keywords: ***$Znnni_3$, Antiperovskite, Phonon Dispersion, Debye Temperature, Specific Heat.***

I. INTRODUCTION

In last few years an intensive research effort has emerged that aims at identifying and characterizing relatively low T_c superconductors that are exotic in their nominal state properties and order parameters symmetry. Since the unexpected appearance of superconductivity having $T_c \sim 8$ K for Ni- rich ternary carbide $MgCNi_3$ with cubic antiperovskite-like structure [1], a much interest have been paid in the scientific community to other related materials. The nature of the superconducting state in these compounds is controversial and remains an open problem [2-4]. Due to understand the origin of exact nature of superconductivity, the researches of a set of ternary carbon containing antiperovskite $MgCNi_3$ has been performed intensively [5-17]. A detail study of the properties of $MgCNi_3$ and related antiperovskite-type carbides [18-22] and efforts to improve their properties through their chemical substitution [23-26] have also been carried out.

Recently, the discovery of a new carbon free superconductor $ZnNNi_3$ with $T_c \sim 3$ K [27] has been synthesized, which has been successfully prepared by reacting Zn with Ni powders in NH_3 gas [28]. To the best of our knowledge, this is the only Ni-based nitrogen containing superconducting material and is now very intriguing. Further, very recently a set of antiperovskite-like Ni-rich ternary nitrides $MNNi_3$ (M= Zn, Mg, Cd, Al, Ga, and In) has been synthesized

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and characterized by means of band structure calculations [28-37]. Also the optical and mechanical properties of $MNNi_3$ have been calculated theoretically [37].

In order to fully take advantages of the properties of $ZnNNi_3$, a thorough investigation of its phonon and thermodynamic properties is necessary. Further, understanding on the relationship between superconductivity and ferromagnetism in Ni-based antiperovskite superconductor, it is necessary to synthesize as many as new materials. The calculations of phonon and thermodynamic properties of solids, surfaces and nanocrystals play an important role in the structural characterization of matter. As far as we know no attempt has been made to calculate the phonon and thermodynamic properties of superconducting $ZnNNi_3$. In view of the above circumstances, we report a detailed study of phonon and thermodynamic properties of superconducting $ZnNNi_3$.

II. METHOD OF CALCULATIONS

The calculations are performed using the first-principle pseudopotential method in the framework of density functional perturbation theory (DFPT) with local density approximation (LDA) as implemented in CASTEP code [38]. Atomic pseudopotentials are generated separately for atoms Zn, N, and Ni by using the $3d^{10}4s^2$, $2s^22p^3$, and $3d^84s^2$ atomic configuration respectively. A 4×4×4 Monkhorst-Pack grid is chosen for k-grid sampling in the Brillouin zone integration. The plane-wave cut off energy is taken as 860 eV. The Ni-based $ZnNNi_3$ superconductor adopts a cubic structure consisting of Zn atoms at the corners, N at the body center, and Ni at the face centers of the cube.

III. RESULTS AND DISCUSSION

3.1 Phonon properties

In order to calculate the phonon dispersion spectra of $ZnNNi_3$, we have used density functional perturbation theory (DFPT). The phonons in the $ZnNNi_3$ have been calculated to check whether softening of acoustic phonon are there or not in some crystal symmetry directions as it is supposed to be connected to phase change in this compound. The phonon dispersion spectra of $ZnNNi_3$ along the principle symmetry direction of the Brillouin zone are displayed in Fig. 1. The primitive cell of $ZnNNi_3$ consists of five atoms; the corresponding number of phonon modes is 15, where 3 of acoustics and the remaining 12 are the optic modes. Due to large difference in mass, the phonon dispersion curves of $ZnNNi_3$, decomposes into two well separated parts, a low frequency region with predominantly Zn and Ni atoms and the vibration of the light N atom in high frequency region. So a clear gap is formed between them, as seen in Fig. 1.

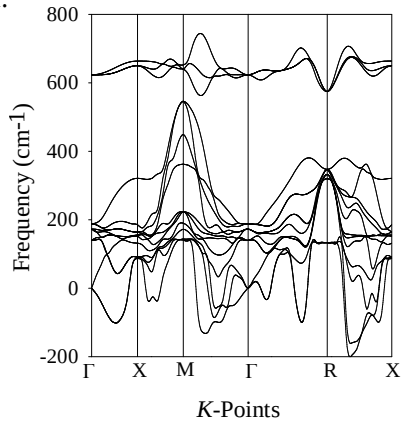

Fig. 1. Phonon dispersion curves of $ZnNNi_3$.

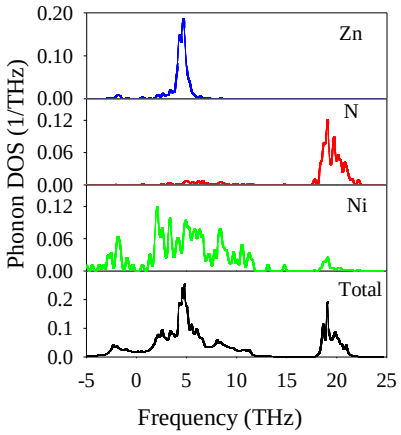

Fig. 2. Total and partial phonon density of States of $ZnNNi_3$.

In Fig. 2, total and partial phonon density of states (PPDOS) of $ZnNNi_3$ is shown. We see that the top most region about 623.5 cm^{-1} consisting of three phonon branches are due to N atom vibrations, the middle and lower twelve branches are due to Zn and Ni atom vibrations. It is well known that the nature of the phase transitions and the dielectric and piezoelectric responses of a compound are determined from the unstable modes. Unstable mode is one, which has negative frequencies, i.e. their dispersion is shown below the zero frequency line. In the present study, the negative frequency is observed in $ZnNNi_3$ as shown in Fig. 1, which is the clear indication of the lattice dynamical instability. Also it is seen from the PPDOS that the unstable mode arises due to the vibrations of Ni atom. While such soft phonon modes are noted before on complex oxide ferroelectrics, such as $Pb(Zr, Ti)O_3$, $BaTiO_3$ and $KNbO_3$ [39-41]. The present results show the similar behavior in comparison with the oxide ferroelectrics.

3.2 Thermodynamic properties

Structural phase transitions and thermodynamic properties in condensed matter and materials science research play an important role on applications, as well as in interdisciplinary research. Recently, a growing interest in the field of thermodynamic properties of solids has been paid due to the development of advanced experimental and modeling tools.

The Debye temperature is an important physical quantity which is used to describe the different phenomena in solids such as lattice vibration, elastic constant, specific heat and melting point. The Debye temperature can be calculated from the average sound velocity (v_m), by the following equation [42]:

$$\theta_D = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{\frac{1}{3}} v_m \quad \text{.....(1)}$$

Where h is the Planck's constant; k is the Boltzmann's constant; N_A is the Avogadro's number; ρ is the density; M is the molecular weight, and n is the number of atoms in the formula unit. v_m is defined as [43]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}} \quad \text{.....(2)}$$

Where v_l and v_t represents the longitudinal and transverse sound velocity, respectively, which can be obtained by the shear modulus (G) and Bulk modulus (B) [42]:

$$v_l = \left(\frac{B+\frac{4}{3}G}{\rho}\right)^{\frac{1}{2}} \quad \text{.....(3)}$$

$$v_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \quad \text{.....(4)}$$

In table 1, Debye temperature, longitudinal and transverse sound velocities are displayed. Unfortunately, as far as we know, there are no experimental or theoretical data on these properties of $ZnNNi_3$. Future experiment will test our results.

Table 1: Bulk modulus (B), Shear modulus (G), Longitudinal sound velocity (v_l), Transverse sound velocity (v_t), average sound velocity (v_m) and Debye temperature (θ_D) of $ZnNNi_3$.

Parameter	B (GPa)	G (GPa)	v_l (ms^{-1})	v_t (ms^{-1})	v_m (ms^{-1})	θ_D (K)
Value	195.1	48.43	5853	2527	2855	384

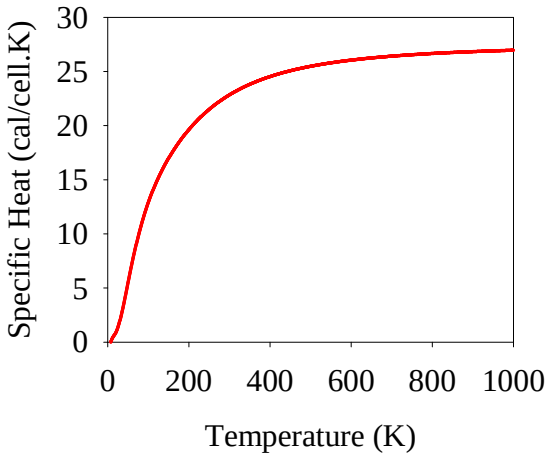

Fig. 3. Temperature dependence of specific heat of $ZnNNi_3$.

Specific heat is a measure of energy that a substance can absorb or emit in a given period of time. The molar specific heats of most solids at room temperature and above are nearly constant, in agreement with the Law of Dulong and Petit. At lower temperatures the specific heats drop as quantum processes become significant. The low temperature behavior is described by the Einstein-Debye mode l of specific heat. The contribution of specific heat capacity from the lattice vibrations of $ZnNNi_3$ are illustrated in Fig. 3. At temperatures $T \gg \theta_D$ the specific heat agrees with Dulong and Petit's law ($C_v \sim 3R$) [44]. At $T \ll \theta_D$ the specific heat is proportional to T^3. It indicates that the atomic interaction of $ZnNNi_3$ occurs at low temperature.

IV. CONCLUSIONS

In summary, we have carried out a detailed investigation of phonon and thermodynamic properties of $ZnNNi_3$ from first principles. The analysis reveals that this material is not dynamically stable. In particular, the softening of phonons and instability of modes are the features which are supposed to be connected to phase transitions in this compound. The specific heat is also calculated as a function of temperature. Since there are no experimental and theoretical data available for these quantities, we think that the ab initio theoretical estimation is only the reasonable tool obtaining such important information. It is expected that our calculations should motivate experimental and other theoretical study on this compound.

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REFERENCES

[1] T. He, Q. Huang, A.P. Ramirez, Y. Wang, K.A. Regan, N. Rogado, M.A. Hayward, M.K. Haas, J.S. Slusky, K. Inumara, H.W. Zandbergen, N.P. Ong, R.J. Cava, "Superconductivity in the non-oxide perovskite $MgCNi_3$", Nature 411, 2001, 54.

[2] P. M. Singer, T. Imai, T. He, M. A. Hayward, and R. J. Cava, "C^{13} NMR Investigation of the superconductor $MgCNi_3$ up to 800 K". Phys. Rev. Lett. 87, 2001, 257601.

[3] Z. Q. Mao, M. M. Rosario, K. D. Nelson, K. Wu, I. G. Deac, P. Schiffer, Y. Liu, T. He, K. A. Regan, and R. J. Cava, "Experimental determination of superconducting parameters for the intermetallic perovskite superconductor $MgCNi_3$", Phys. Rev. B 67, 2003, 094502.

[4] J. Y. Lin, P. L. Ho, H. L. Huang, P. H. Lin, Y. L. Zhang, R. C. Yu, C. Q. Jin, and H. D. Yang, "BCS-like superconductivity in $MgCNi_3$", Phys. Rev. B 67, 2003, 052501.

[5] M. S. Park, J. S. Giim, S. H. Park, Y. W. Lee, S. I. Lee, E. J. Choi, "Physical properties of $ZnCNi_3$: comparison with superconducting $MgCNi_3$", Supercond. Sci. Technol. 17, 2004, 274.

[6] R. E. Schaak, M. Avdeev, W.-L. Lee, G. Lawes, H. W. Zandbergen, J. D. Jorgensen, N. P. Ong, A. P. Ramirez, R. J. Cava, "Formation of transition metal boride and carbide perovskites related to superconducting $MgCNi_3$", J. Solid State Chem. 177, 2004, 1244.

[7] A. F. Dong, G. C. Che, W. W. Huang, S. L. Jia, H. Chen, Z. X. Zhao, "Synthesis and physical properties of $AlCNi_3$" Physica C 422 , 2005, 65.

[8] P. Tong, Y. P. Sun, X. B. Zhu, W. H. Song, "Strong electron-electron correlation in the antiperovskite compound $GaCNi_3$" Phys. Rev. B 73, 2006, 245106.

[9] M. Uehara, T. Amano, S. Takano, T. Kori, T. Yamazaki, Y. Kimishima, "Chemical pressure effect on the superconductor $MgCNi_3$", Physica C 440 2006, 6.

[10] M. Uehara, T. Yamazaki, T. Kori, T. Kashida, Y. Kimishima, I. Hase, "Superconducting Properties of $CdCNi_3$" J. Phys. Soc. Jpn. 76, 2007, 034714.

[11] P. Tong, Y. P. Sun, X. B. Zhu, W. H. Song, "Synthesis and physical properties of antiperovskite-type compound $In_{0.95}CNi_3$" Solid State Commun. 141, 2007, 336.

[12] M. D. Johannes, W. E. Pickett, "Electronic structure of $ZnCNi_3$" Phys. Rev. B 70 , 2004, 060507.

[13] I. R. Shein, A. L. Ivanovskii, "Electronic and elastic properties of non-oxide anti-perovskites from first principles:Superconducting $CdCNi_3$ in comparison with magnetic $InCNi_3$" Phys. Rev. B 77 , 2008, 104101.

[14] I. R. Shein, V. V. Bannikov, A. L. Ivanovskii, "Structural, elastic and electronic properties of superconducting anti-perovskites $MgCNi_3$, $ZnCNi_3$ and $CdCNi_3$ from first principles" Physica C 468 , 2008, 1.

[15] V. V. Bannikov, I. R. Shein, A. L. Ivanovskii, **"**Band structure, elastic and magnetic properties, and stability of antiperovskites $MCNi_3$ (M = Y − Ag) according to FLAPW-GGA calculations**"** Phys. Solid State 49 , 2007, 1704.

[16] A. F. Dong, G. C. Che, W. W. Huang, "Synthesis and physical properties of $AlCNi_3$"Physica C 422 , 2005, 65.

[17] V. V. Bannikov, I. R. Shein, A. L. Ivanovskii, "Structural, electronic, and magnetic properties of $CaCNi_3$, $SrCNi_3$, and $BaCNi_3$antiperovskites in comparison to superconducting $MgCNi_3$" J. Struct. Chem 51 , 2010, 170.

[18] A. L. Ivanovskii, "Band structure and properties of superconducting MgB_2 and related compounds (A review)" Phys. Solid State 45 ,2003, 1829.

[19] S. Mollah, "The physics of the non-oxide perovskite superconductor $MgCNi_3$" J. Phys. Condens. Matter 16 , 2004, R1237.

[20] D. J. Singh, I. I. Mazin, "Superconductivity and electronic structure of perovskite $MgCNi_3$" Phys. Rev. B 64 , 2001, 140507.

[21] I. R. Shein, A. L. Ivanovskii, N. I. Medvedeva, "Electronic structure of the new $MgCNi_3$ superconductor and related intermetallic compounds" JETP Lett. 74 , 2001, 122.

[22] I. R. Shein, A. L. Ivanovskii, "Energy Bands and Chemical Binding in $MgCNi_3$ Superconductor" J. Struct. Chem. 43 ,2002, 168.

[23] L. Shan, K. Xiz, Z. Y. Liu, H. H. Wen, Z. A. Ren, G. C. Che, Z. X. Zhao, "Influence of carbon concentration on the superconductivity in MgC_xNi_3" Phys. Rev. B 68 , 2003, 024523.

[24] I. R. Shein, A. L. Ivanovskii, E. Z. Kurmaev, A. Moewes, A. Chiuzbian, L. D. Finkelstein, M. Neumann, Z. A. Ren, G. C. Che, "Effect of Co doping on the electronic structure of $MgCNi_3$" Phys. Rev. B 66 , 2002, 024520.

[25] J. L. Wang, Y. Xu, Z. Zeng, Q. Q. Zheng, H. Q. Lin, "Electronic structure of $MgCNi_{3-x}TM_x$ (TM=Cu,Co,Mn)" J. Appl. Phys. 91 , 2002, 8504.

[26] I. G. Kim, J. I. Lee, A. J. Freeman, "Effects of d-band hole doping on electronic structure, magnetism, and superconductivity in Fe- and Co-doped $MgCNi_3$" Phys. Rev. B 65 , 2002, 064525.

[27] M. Uehara, A. Uehara, K. Kozawa, Y. Kimishima, "New Antiperovskite-Type Superconductor $ZnNyNi_3$" J. Phys. Soc. Jpn. 78 , 2009), 033702.

[28] H. Tutuncu, G. P. Srivastava, "Electronic structure, phonons and electron–phonon interaction in $MgXNi_3$ (X = B, C and N)" J. Phys: Condens. Matter 18 , 2006, 11089.

[29] A. B. Karki, Y. M. Xiong, D. P. Young, P. W. Adams, "Superconducting and magnetotransport properties of $ZnNNi_3$ microfibers and films", Phys. Rev. B 79 , 2009 , 212508.

[30] J. H. Shim, S. K. Kwon, B. I. Min, "Electronic structures of antiperovskite superconductors $MgXNi_3$ (X=B, C, and N)". Phys. Rev. B 64 ,2001, 180510.

[31] W. H. Cao, B. Hea, C. Z. Liao, L. H. Yang, L. M. Zeng, C. Dong, "Preparation and properties of antiperovskite-type nitrides: $InNNi_3$ and $InNCo_3$" J. Solid State Chem. 182 , 2009, 3353.

[32] C. Li, W. G. Chen, F. Wang, S. F. Li, Q. Sun, S. Wang, Y. Jia, "First-principles investigation of mechanical and electronic properties of $MNNi_3$ (M=Zn, Mg, or Cd)". J. Appl. Phys. 10 , 2009, 123921.

[33] I. R. Shein, V. V. Bannikov, A. L. Ivanovskii, "Elastic and electronic properties of the new perovskite-like superconductor $ZnNNi_3$ in comparison with $MgCNi_3$" Phys. Status Solidi B 247, 2010, 72.

[34] C. M. I. Okoye, "Structural, elastic and electronic properties of new antiperovskite-type superconductor image from first-principles" Physica B 405, 2010, 1562.

[35] Z. F. Hou, "Elastic properties and electronic structures of antiperovskite-type $InNCo_3$ and $InNNi_3$" cod-mat/arXiv:1002:1124.

[36] V. V. Bannikov, I. R. Shein, A. L. Ivanovskii, "Elastic properties of antiperovskite-type Ni-rich nitrides $MNNi_3$ (M=Zn, Cd, Mg, Al, Ga, In, Sn, Sb, Pd, Cu, Ag and Pt) as predicted from first-principles calculations". Physica B 405, 2010, 4615.

[37] M. A. Helal, A. K. M. A. Islam, "Elastic, electronic and optical properties of hypothetical $SnNNi_3$ and $CuNNi_3$ in comparison with superconducting $ZnNNi_3$" Physica B 406 , 2011, 4564.

[38] S. J. Clark, M. D. Segall, M. J. Probert, C. J. Pickard, P. J. Hasnip, M. C. Payne, "First principles methods using CASTEP" Z. Kristallogr. 220, 2005, 567.

[39] D. J. Singh, L. L. Boyer, "First principles analysis of vibrational modes in $KNbO_3$" Ferroelectrics 136, 1992, 95.

[40] G. Samara, "Pressure and Temperature Dependence of the Dielectric Properties and Phase Transitions of the Antiferroelectric Perovskites: $PbZrO_3$ and $PbHfO_3$". Phys. Rev. B 1, 1970, 3777.

[41] M. Fornari, D. J. Singh, "Possible coexistence of rotational and ferroelectric lattice distortions in rhombohedral $PbZr_xTi_{1-x}O_3$". Phys. Rev. B 63, 2001, 092101.

[42] O. L. Anderson, "A simplified method for calculating the Debye temperature from elastic constants" J. Phys. Chem. Solids 24,1963, 909.

[43] E. Schreiber, O. L. Anderson, N. Soga, in: Elastic constants and their measurements, McGraw-Hill, New York, 1973.

[44] A.T. Petit, P. L. Dulong, (1819). "Recherches sur quelques points importants de la Théorie de la Chaleur". Annales de Chimie et de Physique (in French) 10: 395–413.