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Study of Phonons in the Novel Antiperovskite $ZnCNi_3$

M.M. SINHA
Department of Physics, Sant Longowal Institute of Engineering and Technology
Longowal-148 106, India

The discovery of superconductivity in $MgCNi_3$ has generated a new puzzle in the recent series of found superconductors. Despite its relatively low T_c *ca.* 8K, the presence of Ni signals the possible importance of correlation effects which makes the physics of the pairing mechanism relevant to the famous high T_c cuprates and brings the discussion of unconventional non-electron phonon mechanism. $ZnCNi_3$ is very similar to $MgCNi_3$ structurally and having Tc *ca.* 2K. The lack of superconductivity transition down to 2K is quite unexpected. Understanding why superconductivity is seen in one compound but not the other could be important in resolving the unusual behavior of $MgCNi_3$. It is, therefore, in the present work, the phonons in $ZnCNi_3$ is investigated by applying a de Launey angular force constant model. In this model, the relative displacement of the reference atom and one of its neighbors is considered. The calculated zone center phonons and phonon dispersion curves of $ZnCNi_3$ in the symmetric directions are compared with recently calculated values of $MgCNi_3$ in order to find the mechanism of superconductivity in these compounds.

Key Words: Lattice dynamics, Zone center phonons, Phonon dispersion curves, $MgCNi_3$, $ZnCNi_3$

INTRODUCTION

Intermetallic compounds have been the source of many superconducting materials in the past, but they have been eclipsed in recent years by the perovskite oxides. The recent discovery of superconductivity in MgB_2[1] suggests that intermetallic compounds with simple structure types are worth serious reconsideration as sources of new superconducting materials. The superconductivity at 8 K in antiperovskite compound $MgCNi_3$ has drawn lots of attentions owing to the high nickel content which may complicate the origin of superconductivity and being a possible link between the traditional intermetallic superconductors and the high T_c oxide ones[2]. It has been theoretically suggested to be an unconventional superconductor and near the instability to the ferromagnetism[3]. Experimentally, the pairing mechanism of $MgCNi_3$ is quite controversial. The London penetration depth[4], critical current behaviour[5], and the earlier tunneling spectra[6] suggested an unconventional pairing state. While the NMR relaxation rate[7] specific heat data[8] and the latter tunneling spectra[9] support a conventional s-wave BCS type behavior. So far there are many investigations on the doping effects in $MgCNi_3$. Except for Ni-site

doping with Fe, which causes an increase in Tc followed by a decrease with further doping, other doping experiments at either Ni-site[10-13], or Mg-site[14] or C-site[15] are found to suppress the superconductivity in various ways. In addition, the properties of MgC_xNi_3 are very sensitive to the carbon concentration x. The superconductivity disappears when $x \leq 0.88$[16]. The band structure calculation[17] indicates that as x decreases in MgC_xNi_3, the proximity to ferromagnetism increases, and the increasing spin fluctuations may be responsible for the reduction of T_c. However the specific heat studies suggest that a lowering of x can reduce the strength of both electron-phonon (e-p) coupling and spin fluctuations and the weakening of e-p coupling would lead to a decrease in T_c[18,19]. The physics of $MgCNi_3$ is far away from being thoroughly understood at present, therefore, more efforts are needed.

Alternatively, the study on the closely related compounds is of interest for pursuing new phenomenon, *e.g.*, superconductivity, as well as for understanding the interplay between superconductivity and ferromagnetism in $MgCNi_3$. Recently, the synthesis of $ZnCNi_3$ has been reported by Park *et al.*[20]. Since, $ZnCNi_3$ is very similar to $MgCNi_3$ structurally, and electronically[21], the lack of a superconducting transition down to 2 K is quite unexpected. Understanding why superconductivity is seen in one compound but not the other could be important in resolving remaining questions about the unusual behavior of $MgCNi_3$. Till date there is no study of phonons in the isostructural compound $ZnCNi_3$ and therefore in this paper, the phonon dispersion of $ZnCNi_3$ is sutided by taking the same interatomic interactions for the calculation of phonons in $MgCNi_3$[22].

Crystal structure

The crystal structure of $MgCNi_3$ is structurally fully analogous to familiar oxide perovskites like $CaTiO_3$, and to superconducting perovskite oxides like $(Ba,K)BiO_3$. It was found that $ZnCNi_3$ is isostructural with $MgCNi_3$[20]. ZnCNi3 has the cubic perovskite-like structure (space group Pm3m) consisting of Zn at the corners, C at the body center, and Ni at the face centers of the cube. The atomic positions are Ni: 3 (0.5,0.5,0); Zn: 1a (0,0,0); C: 1b (0.5,0.5,0.5). From the point of view of lattice dynamics, the unit cell contains five atoms give rise to 15 phonons (three acoustics and 12 optic). The symmetry of these phonons at the Γ point (in terms of the O_h representation) is

$$\Gamma\,(O_h) = 4T_{1u} + T_{2u}$$

Where T_{1u} and T_{2u} represent the normal modes with triple degeneracy. One T_{1u} mode is acoustic and the rest are optical modes. The T_{2u} mode is inactive, while T_{1u} modes are only IR active. The compound in cubic phase has no Raman mode.

Methodology

In the present investigation, de Launey angular force (DAF) constant model[23] has been used to study the phonons in the intermetallic compound $ZnCNi_3$. In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used for the various categories of neighbors and the net force on the reference atom is obtained by summing over the contribution from all the neighbors. The present calculation involves four central force constants α_1, α_2, α_3, α_4 and four angular force constants α_1', α_2', α_3' and α_4' between C-Ni, Zn-Ni, Zn-C and Ni-Ni atoms respectively up to third nearest neighbor. Till date no experimental or theoretical results of phonons are available in literature. Therefore, in the present investigation, the phonons of $ZnCNi_3$ are calculated first time by taking the force constants as taken for $MgCNi_3$ in my earlier study[22] and are listed in table 1.

TABLE-1
VALUES OF FORCE CONSTANTS (n m^{-1})

Force constant	$ZnCNi_3$/$MgCNi_3$
α_1 (C–Ni)	19.1
α_1' (C-Ni)	19.0
α_2 (Zn-Ni)	-2.5
α_2' (Zn-Ni)	8.3
α_3 (Zn–C)	30.0
α_3' (Zn–C)	4.5
α_4 (Ni-Ni)	10.0
α_4' (Ni-Ni)	-1.0

TABLE-2
CALCULATED ZONE CENTER PHONON FREQUENCIES (cm^{-1})

ZC- Phonons	$ZnCNi_3$	$MgCNi_3$
T_{1u}	570	594
T_{1u}	206	285
T_{1u}	174	180
T_{2u}	131	130

Taking these force constants as input parameters, the dynamical matrix is solved at the ZC as well as along three symmetric directions [k00], [kk0] and [kkk]. The ZC phonons thus obtained are listed in

table 2. The phonon dispersion curves are calculated in three symmetric directions and are shown in Fig. 1.

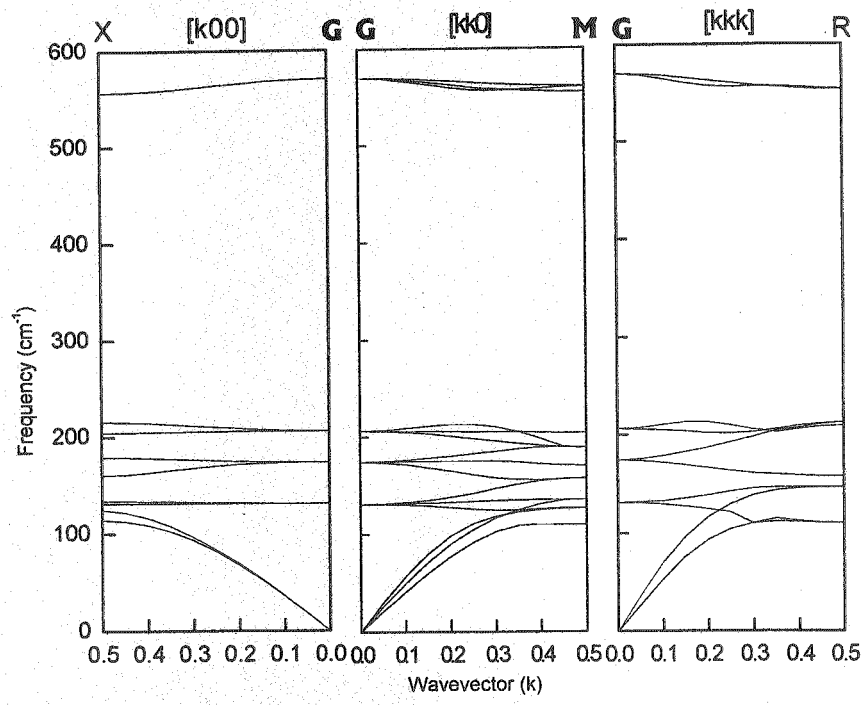

Fig. 1. Photon dispersion of $ZnCNi_3$

RESULTS AND DISCUSSION

Due to large differences in mass, the phonon dispersion curves (PDC) of $ZnCNi_3$ (Fig. 1) decomposes into two well separated parts, a low-frequency region with predominantly Ni and Zn modes and the vibration of the light C atom around 570 cm^{-1}. It is obvious from Fig. 1 that phonon branches are distributed almost uniformLy up to about 200 cm^{-1} in all symmetric directions. The phonon dispersion curves of $ZnCNi_3$ along all three symmetric directions are very similar to that of $MgCNi_3$[22]. The calculated eigen frequencies and eigen vectors suggest that the top most region about 570 cm^{-1} consisting of three phonon branches are due to carbon atom vibrations, the middle three branches at about 206 cm^{-1} are due to Zn atom vibrations, and the lower nine branches are due to Zn and Ni atom vibrations. A similar description of the phonon dispersion has been given by Ignitov *et al.*[24] from their DFT calculation and Jha[25] from his rigid ion model calculation for $MgCNi_3$. The main issue of present calculation is to understand why superconductivity is seen in one compound ($MgCNi_3$) but not in the isostructural compound ($ZnCNi_3$). The present investigation does not show the occurrence of softening of acoustical modes at the boundary of Brillouin Zone (BZ) along major symmetry directions and similar results were also obtained in our calculation for $MgCNi_3$[22]. Whereas softening was observed in $MgCNi_3$ compound by other calculations[24,25]. The softening of phonons and

instability of modes are the features, which are supposed to be connected to superconductivity in these compounds. It is also obvious from Fig.1 that the dispersion of branch around (206 cm^{-1}), due to vibration of Zn atoms, is quite low in all direction whereas these branches have significant dispersion for $MgCNi_3$[22]. This is due to heavy mass of Zn than Mg as corresponding branches are due to vibration of Zn/Mg atoms. Obviously, the important role in the observed non-superconducting state in $ZnCNi_3$ will belong to the changes in phonon frequencies. The softening of phonons in any symmetric direction is missing from the present analysis. The possible softening and anharmonic effects highly motivate further experimental and theoretical studies.

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