Phonons in non-oxide perovskite superconductor MgCNi$_3$

M M Sinha
Department of Physics, Sant Longowal Institute of Engineering and Technology, Longowal, Distt. Sangrur (Punjab) 148 106
E-mail: mm_sinha@rediffmail.com

Received 1 March 2006; revised 25 July 2006; accepted 23 October 2006

The new intermetallic non-oxide perovskite superconductor MgCNi$_3$ was discovered by He et al., Nature, 411(2001) 54, following on from the breakthrough of the finding of the MgB$_2$ superconductor at the beginning of 2001. MgB$_2$ has subsequently been intensively studied; however, less attention has been paid to MgCNi$_3$ due to its much lower superconducting transition temperature ($T_c$ ~8 K), as compared to that of MgB$_2$ ($T_c$ ~39 K). But it has many interesting properties, which need to be focused on to obtain an understanding of its complicated physics. Being a perovskite superconductor like Ba$_{1-x}$K$_x$BiO$_3$ and cuprate superconductors, MgCNi$_3$ is special as it is neither an oxide nor does it contain any copper. Meanwhile, MgCNi$_3$ can be regarded as fcc Ni with only one quarter of Ni replaced by Mg and with C sitting on the octahedral sites. The fact that superconductivity rather than ferromagnetism occurs in a compound where so much nickel is present is surprising and suggest that MgCNi$_3$ is a candidate for exhibiting unconventional superconductivity. In this work, a de Launey angular force constant model has been used to study the phonons in MgCNi$_3$. The phonon dispersion curves in the symmetric directions are plotted and compared with available results.

Keywords: Lattice dynamics, Phonon spectra, Zone center phonons, Intermetallic compound

IPC Code: H01L 39/00

1 Introduction

The appearance of superconductivity near 8 K in the Ni-rich perovskite, MgCNi$_3$, has stimulated much interest not only because it is unusual in a compound that is primarily Ni, but because the exact nature of the superconducting state and its microscopic origins are still being debated. It is expected that this compound is near a ferromagnetic instability which might be reached by hole doping on the Mg sites$^2$. The possibility of unconventional superconductivity due to the proximity of these two types of collective order has attracted great interest for the present study. Temperature dependence of specific heat$^3$ and the observation of Hebel-Slichter peak in NMR measurement$^4$ suggested that MgCNi$_3$ is a conventional BCS superconductor. On the other hand, some non-s-wave features were reported from a tunneling measurement$^5$ and a microwave impedance measurement$^6$. For instance, the temperature dependence of penetration depth observed in Ref. [6] is inconsistent with isotropic s-wave BCS pairing, but can be interpreted as a signature of nodal gap symmetry. The nature of superconductivity in MgCNi$_3$ is, thus, still controversial. Recently, Voelker and Sigrist$^7$ suggested a theoretical picture which presents a possible explanation of these seemingly contradicting experimental results. There it was assumed that MgCNi$_3$ is a multiband material which superconducts by the conventional BCS mechanism. Then, due to the multiband structure and a possible interaction between the bands, MgCNi$_3$ can exhibit an unconventional symmetry of superconducting order parameter and consequently non-BCS like behaviour. There are still open questions regarding the role of spin fluctuations and/or lattice instabilities on the origin of superconductivity in this system.

Since MgCNi$_3$ bears similarity to superconducting nickel borocarbides (RENi$_2$B$_2$C, RE = Y, Lu, where RE stands for rare earth) where for the Y and Lu compounds an acoustic phonon branch exhibits a pronounced softening at lower temperatures$^{8,10}$, a feature which is supposed to be connected to superconductivity in these compounds. Hints for unusual lattice dynamical properties of MgCNi$_3$ have been inferred from a recent X-ray absorption study, which indicated deviations of the local atomic structure from the ideal perovskite lattice at temperatures$^{11}$ below 70 K and from a very recent linear muffin-tin orbitals (LMTO) calculation of the harmonic phonons$^{12}$ of MgCNi$_3$ which found a dynamical instability of the stoichiometric compound. In this paper, a de Launey angular force constant model$^{13}$ has been used for detailed study of the phonons in MgCNi$_3$. 
2 Crystal Structure
The crystal structure of MgCNi$_3$ (Figure 1) is structurally fully analogous to familiar oxide perovskites like CaTiO$_3$, and to superconducting perovskite oxides like (Ba,K)BiO$_3$. MgCNi$_3$ has the cubic perovskite-like structure (space group Pm3m) with a lattice constant $a = 3.81\text{Å}$ and consisting of Mg 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); Mg: 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 $\Gamma$ 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.

3 Present Approach
In the present investigation, a de Launey angular force (DAF) constant model\textsuperscript{13} has been used to study the phonons in the intermetallic compound MgCNi$_3$ to check whether softening of acoustic phonons are there or not in some crystal symmetry directions as it is supposed to be connected to superconductivity in these compounds. In DAF model, the relative displacement of the reference atom and one of the neighbours 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 neighbours are calculated separately and summed up together. Different force constants are used for the various categories of neighbours and the net force on the reference atom is obtained by summing over the contribution from all the neighbours. The present calculation involves four central force constants $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$ and four angular force constants $\alpha_1'$, $\alpha_2'$, $\alpha_3'$ and $\alpha_4'$ between C-Ni, Mg-Ni, Mg-C and Ni-Ni atoms respectively up to third nearest neighbour. The calculated dynamical matrix of (15×15) is reduced to three matrices of the order (5×5) at zone center (ZC). Till date no experimental IR active phonon modes are available in literature. Recently Heid et al\textsuperscript{14}, and Ignatov et al\textsuperscript{12} have calculated phonon dispersion curves of MgCNi$_3$ by using perturbation approach\textsuperscript{15} and LMTO methods, respectively. Both methods have predicted same zone center (ZC) frequencies for three IR active modes except one. The LMTO calculations predict significantly higher frequency for the Mg modes (at $\approx 45$ meV) to that predicted by Heid et al\textsuperscript{14} at 35 meV at ZC. In the present calculation, the interatomic force constants are obtained by fitting the calculated results of Heid et al\textsuperscript{14} at the ZC for infrared active phonon frequencies. The force constants thus calculated are listed in Table 1. 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 [k0k]. The ZC phonons thus obtained are listed in Table 2. The phonon dispersion curves thus obtained in three symmetric directions are shown in Figure 2.

4 Results and Discussion
It is clear from Table 1 that the calculated force constant $\alpha_3$ between Mg-C is the strongest among all other interatomic interactions and is followed by $\alpha_1$ (C-Ni). This suggests that the covalent bonding between (Mg-C) is the strongest than that between (C-Ni), (Ni-Ni) and (Mg-Ni). Due to large differences in

---

Table 1—Values of force constants (N m$^{-1}$)

<table>
<thead>
<tr>
<th>Force constant</th>
<th>MgCNi$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$, (C-Ni)</td>
<td>19.1</td>
</tr>
<tr>
<td>$\alpha_1$, (C-Ni)</td>
<td>19.0</td>
</tr>
<tr>
<td>$\alpha_2$, (Mg-Ni)</td>
<td>-2.5</td>
</tr>
<tr>
<td>$\alpha_2$ (Mg-Ni)</td>
<td>8.3</td>
</tr>
<tr>
<td>$\alpha_3$ (Mg-C)</td>
<td>30.0</td>
</tr>
<tr>
<td>$\alpha_3$ (Mg-C)</td>
<td>4.5</td>
</tr>
<tr>
<td>$\alpha_4$ (Ni-Ni)</td>
<td>10.0</td>
</tr>
<tr>
<td>$\alpha_4$ (Ni-Ni)</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

---

Fig. 1—The crystal structure of the intermetallic compound MgCNi$_3$. 
mass, the phonon dispersion curves (PDC) of MgCNi$_3$ (Figure 2) decomposes into two well separated parts, a low-frequency region with predominantly Ni and Mg modes and the vibration of the light C atom around 594 cm$^{-1}$. It is obvious from Figure 2 that phonon branches are distributed almost uniformly up to about 200 cm$^{-1}$ in all symmetric directions. The PDC shows that there are three regions in which phonon modes are distributed. The calculated eigen frequencies and eigen vectors suggest that the topmost region consisting of three phonon branches are due to carbon atom vibrations, the middle three branches at about 285 cm$^{-1}$ are due to Mg atom vibrations, and the lower nine branches are due to Mg and Ni atom vibrations. A similar description of the phonon dispersion has been given by Ignitov et al$^{12}$. from their DFT calculation and Jha$^{16}$ from his rigid ion model calculation. The main issue of the present calculation is to verify the occurrence of softening of acoustical modes at the boundary of Brillouin zone (BZ) along major symmetry directions in MgCNi$_3$ compound as obtained by other calculations$^{12,14,16}$. The softening of phonons and instability of modes are the features which are supposed to be connected to superconductivity in these compounds. The present calculation is not able to produce the unstable modes at zone boundary points in [k00], [kk0] and [kkk] directions of BZ. The instability of modes appears over a large area in the reciprocal space by DFT calculation$^{12,14}$. The present calculation gives similar results as obtained by rigid ion model method$^{16}$ along [k00] direction but along other two symmetric directions it is different than that obtained by Jha$^{16}$. Other than acoustic mode instability along [k00] and [kkk], the present analysis gives similar results as calculated by Jha$^{16}$. The softening of phonons in any symmetric direction is missing from the present analysis. The possibility of multi-band superconductivity and possible softening and anharmonic effects highly motivate further experimental and theoretical studies.

References

7. Voelker K, Sigrist M, available from <cond-mat/0208367>