Effect of angular forces on the phonons in LuNi$_2$B$_2$C

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Received 19 November 1996, revised 18 September 1997; accepted 22 September 1997

Abstract

The phonons in rare earth nickel borocarbides are investigated using an angular force model approach. The analytical expressions for the Raman and the infrared frequencies of these compounds have been determined for the first time. A comparison of the expressions of the Raman modes with the expression of the similar modes in Nd$_{2−x}$Ce$_x$CuO$_4$ has been made and the correspondence discussed. It has been observed that the angular forces between Lu and C atoms in Lu–C layer are the most important factor in obtaining a good agreement for the phonons with the experimentally measured inelastic neutron scattering results in the case of LuNi$_2$B$_2$C.

Keywords: Borocarbide superconductors; Raman spectra; Infrared spectra

1. Introduction

Recently, superconductivity has been observed in the quaternary intermetallic rare earth nickel borocarbides [1–4], notably LuNi$_2$B$_2$C and YNi$_2$B$_2$C with superconducting transition temperatures 16.6 and 15.6 K respectively. It has been suggested that superconductivity in these systems can be attributed to a conventional electron–phonon mechanism [5] and hence, the investigation of the phonons will be quite important from the point of view of understanding the mechanism of superconductivity in these borocarbides. An angular force model approach has been used in the present paper to study the phonons in LuNi$_2$B$_2$C. At the zone centre, the analytical expressions for the Raman and the infrared frequencies have been obtained for the first time to give an in-depth knowledge of the interatomic forces present in these nickel borocarbides. The Raman modes expressions were then compared with the corresponding expressions for Nd$_{2−x}$Ce$_x$CuO$_4$ to see the similarity and differences between the two superconducting compounds. It has been found that the sheets B$_2$Ni$_2$ in LuNi$_2$B$_2$C and Nd$_{2−x}$Ce$_x$O$_2$ in Nd$_{2−x}$Ce$_x$CuO$_4$ respectively play a similar role with respect to their phonons. However, the layers Lu–C in LuNi$_2$B$_2$C and Cu–O in Nd$_{2−x}$Ce$_x$CuO$_4$ respectively are different from the point of view of their phonon frequencies. Further, it has been found that the angular forces between the Lu and the C atoms in the Lu–C layer play an important role in determining the phonons in LuNi$_2$B$_2$C. With the inclusion of
central force constants between B–C, Ni–B, Ni–Ni, Lu–C and Lu–B and angular force constant between Lu–C atoms. Good agreement with the experimentally measured phonon frequencies has been obtained.

2. Theory

The structure of body centered tetragonal RNi$_2$B$_2$C (R = rare earth element) is described by space group I4/mmm and is shown in Fig. 1. It consists of R–C layers separated by B$_2$Ni$_2$ sheets. Group theoretical treatment of the optical zone centre phonon modes [6] yields

$$\Gamma = A_{1g} \oplus B_{1g} \oplus 2E_g \oplus 4A_{2u} \oplus 4E_u.$$  \hspace{1cm} (1)

There are four Raman active modes, $A_{1g}$, $B_{1g}$, and $2E_g$, and eight infrared modes, $4A_{2u}$ and $4E_u$, including the acoustical modes.

In the angular force model approach, we have used the deLauney type angular forces [7] along with the central forces. The interatomic interactions are accounted for between atoms B–C ($\alpha_1 - \alpha_1$), Ni–B ($\alpha_2$, $\alpha_2'$), Ni–Ni ($\alpha_3$, $\alpha_3'$), Lu–C ($\alpha_4$, $\alpha_4'$) and Lu–B ($\alpha_5$, $\alpha_5'$). In the brackets, the non-prime force constant is the central whereas the prime force constant is the angular one for each interatomic interaction. There are six atoms in the unit cell. The $18 \times 18$ dynamical matrix was derived and analytically solved at the zone centre to give the following analytical expressions for the frequencies, $\omega$, of the Raman and the infrared modes

For $A_{1g}$:

$$m_n \omega^2 = \alpha_1 + 2\Omega + S.$$  \hspace{1cm} (2)

For $B_{1g}$:

$$m_n \omega^2 = 2\Omega + 8\alpha_3'.$$  \hspace{1cm} (3)

for $E_g$:

$$\begin{vmatrix}
\alpha_1 + 2\alpha_2 + P + R - m_n \omega^2 \\
P - 2\alpha_2' \\
2\alpha_2' + P + 4\alpha_2 + 4\alpha_3 - m_n \omega^2
\end{vmatrix} = 0,$$  \hspace{1cm} (4)
for \( A_{2g} \):

\[
\begin{vmatrix}
4\alpha_4' + 2S - m_{\alpha_4}w^2 & -S & 0 & -4\alpha_4' \\
-2S & \alpha_1 + 2Q + S - m_{\alpha_1}w^2 & -2Q & -2\alpha_1 \\
0 & -2Q & 2Q - m_{\alpha_1}w^2 & 0 \\
-4\alpha_4' & -\alpha_1 & 0 & 2\alpha_1 + 4\alpha_4' - m_{\alpha_1}w^2 \\
\end{vmatrix} = 0. \tag{5}
\]

For \( E_{g} \):

\[
\begin{vmatrix}
2\alpha_4 + 2\alpha_4' + 2P - m_{\alpha_4}w^2 & -R & 0 & -2\alpha_4 - 2\alpha_4' \\
-2R & \alpha_1 + 2\alpha_1' + P - m_{\alpha_1}w^2 & -2\alpha_1' - P & -2\alpha_1 \\
0 & -2\alpha_1' - P & 2\alpha_1' + P - m_{\alpha_1}w^2 & 0 \\
-2\alpha_4 - 2\alpha_4' & -\alpha_1' & 0 & 2\alpha_1' + 2\alpha_4 + 2\alpha_4' - m_{\alpha_1}w^2 \\
\end{vmatrix} = 0. \tag{6}
\]

where \( P = 2\alpha_4' + T(\alpha_2 - \alpha_2'), Q = 2\alpha_4' + U(\alpha_2 - \alpha_2'), \)

\( R = 4\alpha_4' + V(\alpha_3 - \alpha_3'), S = 4\alpha_4' + W(\alpha_3 - \alpha_3'), T = a^2/2(a^2/4 + c^2/64), U = c^2/32(a^2/4 + c^2/64), R = a^2/2(a^2/2 + c^2/64), S = c^2/16(a^2/2 + c^2/64). \)

3. Comparison for the Raman modes between \( \text{LuNi}_2\text{B}_2\text{C} \) and \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \)

Earlier, the analytical expressions for the Raman and the infrared modes were derived \[8\] using an angular

force model approach in case of \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \), which has the same structural space group \( \text{I}4/m \text{mm} \). On comparison, it is observed that the \( \text{B}_2\text{Ni}_2 \) sheets in \( \text{LuNi}_2\text{B}_2\text{C} \) and \( \text{Nd}_{2-x}\text{Ce}_x\text{O}_2 \) in \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) respectively play a similar role with respect to the phonons. In fact, the nickel atoms are symmetrically exactly equivalent to \( \text{O}_2^- \) atoms, whereas boron and lutetium atoms occupy the same symmetry as those of neodymium and copper atoms respectively. The difference lies in the site symmetry of carbon in the \( \text{Lu}^-\text{C} \) layer and oxygen in the \( \text{Cu}^-\text{O} \) sheets. The expressions for \( B_{1g} \) and \( A_{1g} \) are similar for both the structures. If one takes the \( B_{1g} \) measured value as \( 344 \text{ cm}^{-1} \) for \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) \[9\], then a simple transformation \( 344 \times \text{[16 (oxygen atomic mass)/58.71 (nickel atomic mass)]}^{1/2} \) gives a frequency of \( 179.6 \text{ cm}^{-1} \) for \( B_{1g} \) in \( \text{LuNi}_2\text{B}_2\text{C} \), quite in agreement with the observed value of \( 191 \text{ cm}^{-1} \). Similarly, from the \( A_{1g} \) mode of \( 230 \text{ cm}^{-1} \) in \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) \[9\], the transformed value comes out to be \( 230 \times \text{[144.3 (neodymium atomic mass)/10.82 (boron atomic mass)]}^{1/2} = 840 \text{ cm}^{-1} \), again in very good agreement with the measured value of \( 825 \text{ cm}^{-1} \) of \( A_{1g} \) in \( \text{LuNi}_2\text{B}_2\text{C} \). A similar transformation in terms of reduced mass for \( E_g \) modes also provides a fair agreement for the lower \( E_g \) mode. Thus, in case of the two structures under discussion, the Raman modes are quite similar, whereas the infrared modes are found to be different. Eqs. (2)-(4) for the interatomic force constants involved in the Raman modes of \( \text{LuNi}_2\text{B}_2\text{C} \) show that the force constants \( \alpha_4 \) and \( \alpha_4' \) between the \( \text{Lu}^-\text{C} \) atoms in the \( \text{LuC} \) layer do not effect the Raman modes. Hence, it was considered that these force constants \( \alpha_4 \) and \( \alpha_4' \) may

| Table 1 |
|------------------|------------------|
| The interatomic force constants in case of \( \text{LuNi}_2\text{B}_2\text{C} \ (a = 3.464 \AA, c = 10.631 \AA) \) |

<table>
<thead>
<tr>
<th>Force constants (between atoms)</th>
<th>Value (N/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}^-\text{C} )</td>
<td>3.00</td>
</tr>
<tr>
<td>( \text{Ni}^-\text{B} )</td>
<td>0.75</td>
</tr>
<tr>
<td>( \text{Ni}^-\text{Nd} )</td>
<td>0.75</td>
</tr>
<tr>
<td>( \text{Lu}^-\text{C} )</td>
<td>0.45</td>
</tr>
<tr>
<td>( \text{Lu}^-\text{B} )</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{Lu}^-\text{C} )</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table 2
Calculated phonon frequencies corresponding to zone centre infrared active modes in case of LuNi$_3$B$_2$C with and without angular force constant ($\alpha'$) between Lu–C atoms in (q00) direction

<table>
<thead>
<tr>
<th>Wave vector</th>
<th>Angular force constant ($\alpha'$)</th>
<th>Calculated phonon frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0,0</td>
<td>Present</td>
<td>466.6  424.0  102.2  0.0  466.6  424.0  102.2  0.0  1199.0  426.2  122.0  0.0</td>
</tr>
<tr>
<td>0.0,0</td>
<td>Absent</td>
<td>466.3  367.5  102.1  0.0  466.3  367.5  102.1  0.0  1197.0  383.8  52.73  0.0</td>
</tr>
<tr>
<td>0.2,0,0</td>
<td>Present</td>
<td>463.6  419.6  127.2  81.9  466.8  419.6  126.5  78.09  1199.0  426.9  109.1  55.45</td>
</tr>
<tr>
<td>0.2,0,0</td>
<td>Absent</td>
<td>463.5  363.6  126.5  77.02  466.7  363.6  125.6  73.36  1179.0  389.5  73.09  42.83</td>
</tr>
<tr>
<td>0.4,0,0</td>
<td>Present</td>
<td>457.5  411.7  133.5  124.9  468.6  411.7  180.5  126.3  1199.0  423.6  101.6  86.46</td>
</tr>
<tr>
<td>0.4,0,0</td>
<td>Absent</td>
<td>457.5  356.5  132.9  114.8  468.6  356.5  180.4  115.7  1179.0  388.1  89.40  44.51</td>
</tr>
<tr>
<td>0.6,0,0</td>
<td>Present</td>
<td>458.3  411.7  135.4  118.2  468.5  411.7  179.9  126.7  1199.0  409.6  127.9  76.49</td>
</tr>
<tr>
<td>0.6,0,0</td>
<td>Absent</td>
<td>458.3  356.5  132.9  114.8  468.5  356.5  179.9  115.7  1179.0  388.1  89.40  44.51</td>
</tr>
<tr>
<td>0.8,0,0</td>
<td>Present</td>
<td>471.7  419.7  141.8  87.31  465.8  419.7  145.7  90.89  1199.0  401.4  122.4  66.03</td>
</tr>
<tr>
<td>0.8,0,0</td>
<td>Absent</td>
<td>471.6  363.6  145.6  82.03  465.8  363.6  115.7  85.54  1178.0  354.8  112.8  42.28</td>
</tr>
<tr>
<td>1.0,0,0</td>
<td>Present</td>
<td>480.1  424.2  152.7  61.89  480.1  424.2  152.7  61.89  1199.0  409.2  77.64  78.03</td>
</tr>
<tr>
<td>1.0,0,0</td>
<td>Absent</td>
<td>480.0  367.7  152.7  61.88  480.0  367.7  115.7  61.88  1178.0  350.1  77.64  54.75</td>
</tr>
</tbody>
</table>

Fig. 2. Phonon dispersion in LuNi$_3$B$_2$C along the symmetry [q00] and [00q] directions, where x-axis represents the reduced wave vector. The experimental results are from Ref. [11], except for the Raman experimental values which are from Ref. [10].

play an important role in bringing a difference in the infrared modes as compared to the infrared modes in Nd$_{2-x}$Ce$_x$CuO$_4$. This also can be seen from the fact that the carbon site symmetry is different in LuNi$_3$B$_2$C when compared with the oxygen site symmetry in Nd$_{2-x}$Ce$_x$CuO$_4$. In order to confirm that the force constants

\[ [q00] \]

\[ [00q] \]
\( \alpha_1 \) and \( \alpha_2 \) are important, we investigate the phonon spectrum in case of LuNi\(_2\)B\(_2\)C along \([q00]\) and \([00q]\) symmetry directions.

4. Phonon spectrum results and discussion

In order to evaluate the force constants for LuNi\(_2\)B\(_2\)C, initially, the analysis was confined only to central force constants. These central force constants were fit to provide an agreement for the observed Raman modes [6,10] in case of LuNi\(_2\)B\(_2\)C (\(A_{1g} = 825 \text{ cm}^{-1}, B_{1g} = 191 \text{ cm}^{-1}, E_g = 470, 282 \text{ cm}^{-1}\)). The \( A_{1g} \) modes were taken from the results of polycrystalline samples of YNi\(_2\)B\(_2\)C [10]. These force constants are listed in Table 1. Using these force constants, the calculated infrared active modes are given in Table 2 for all symmetry wavevectors in the \((q00)\) direction. The agreement obtained with only the central force constants for Raman modes is quite satisfactory. However, the agreement is not adequate in the case of infrared modes of LuNi\(_2\)B\(_2\)C.

As suggested earlier, an attempt was made to incorporate the angular force constant \( \alpha_2 \) between the Lu–C atoms and it was found that the inclusion of this force constant not only improves the agreement for the infrared modes but also provides a fair agreement for the acoustical and lower optical branches, for which the inelastic neutron scattering results are available [11]. This can be observed from Fig. 2 and Table 2. As is obvious from Table 2, this force constant \( \alpha_2 \) has a large effect on all the acoustical branches, as well as, the lower optical branches, specially corresponding to \( A_{3g} \) infrared mode, where the change is about 50% (from 82.73 cm\(^{-1}\) to 122 cm\(^{-1}\) at the zone centre). It is inferred that the angular force constant between the rare earth and the carbon atom in the Lu–C layer plays an important role in explaining the phonon dispersion in LuNi\(_2\)B\(_2\)C.

References