Theoretical studies of electronic structure, phonon spectrum and electron-phonon interaction in AlCNi$_3$

H M Tütüncü$^1$, S Duman$^1$, S Bağcı$^1$ and G P Srivastava$^2$

$^1$ Sakarya Üniversitesi, Fen-Edebiyat Fakültesi, Fizik Bölümü, 54140, Adapazarı, Turkey
$^2$ School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK
E-mail: gps@excc.ex.ac.uk

Abstract.

We report results of first-principles calculations for structural properties, electronic structure, phonon spectrum and electron-phonon interaction for the antiperovskite compound AlCNi$_3$. The structural properties are calculated using a plane-wave-pseudopotential method and the density functional theory within the generalised gradient approximation. The electronic structure and density of states for AlCNi$_3$ are presented and compared with previous theoretical calculations. Our structural and electronic results are used, within the implementation of a linear response technique, for calculations of phonon states. We have observed that all phonon modes are stable along the [100] direction while unstable phonon modes are found in the [110] and [111] symmetry directions. At the Brillouin zone edge point X, the electron-phonon coupling parameters for phonon modes in AlCNi$_3$ are calculated to be smaller than their corresponding values for MgCNi$_3$. This result indicates that the electron-phonon interaction is not very strong in AlCNi$_3$.

1. Introduction

The inter-metallic non-oxide perovskite structures have attracted much attention due to the discovery of 8 K superconductivity in the non-oxide perovskite MgCNi$_3$. It is surprising that the ground state of MgCNi$_3$ is superconducting, since the Ni content is large (electron-magnon coupling can also be expected [1]). Thus, several attempts have been made to investigate the structural, electronic, vibrational and superconducting properties of MgCNi$_3$ [2]. These studies indicate that MgCNi$_3$ can be described as a BCS-type superconductor due to strong electron-phonon interaction. After the explanation of superconductivity in MgCNi$_3$, it is interesting to study materials which are closely related to MgCNi$_3$, i.e., XCNi$_3$ (X=Al, Ga and Zn) [3, 4, 5]. In particular, a density functional theory [5] has been used to investigate the electronic and optical properties of AlCNi$_3$. On the experimental side, the structural, magnetic, electrical transport, specific heat, thermal and superconducting properties of AlCNi$_3$ have been studied by different groups [3, 4]. These experimental works have pointed out absence of superconductivity in AlCNi$_3$.

Although some progress has been made in theoretical description of the structural, electronic and optical properties of AlCNi$_3$, its vibrational properties are still not established. An accurate description of its vibrational properties is very important for studying electron-phonon interaction. Moreover, the absence of superconductivity in AlCNi$_3$ can be explained clearly if one can calculate the electronic structure, phonon spectrum and electron-phonon interaction for
this material. In this work we provide results of a systematic determination of these properties of \( \text{AlCNi}_3 \) by employing the plane-wave pseudopotential method, density functional theory, and a linear response technique.

2. Theory

Pseudopotential plane-wave \textit{ab initio} calculations were performed within the framework of the density functional theory. Electron-electron interactions are treated within the generalised gradient approximation (GGA) by the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional \cite{6}. We have used the ultrasoft pseudopotentials \cite{7} which have been generated according to a modified Rappe-Rabe-Kaxiras-Joannopoulos scheme \cite{8}. For the Brillouin zone integration, we used a \( 20 \times 20 \times 20 \) \( k \)-points mesh in order to calculate the equilibrium lattice constant and electronic structure. We have studied phonon properties using the density-functional perturbation theory \cite{9}. A \( 16 \times 16 \times 16 \) \( k \)-points grid was used for sampling the Brillouin zone for phonon calculations. Eight dynamical matrices were generated using a mesh of \((4, 4, 4)\) reciprocal lattice divisions. Then, the full phonon dispersion was determined by using the force constants from a discrete Fourier transform of these dynamical matrices. The technique in the calculation of electron-phonon interaction has been described in detail in several previous works \cite{2}. The Fermi-surface sampling for the evaluation of the electron-phonon matrix elements was done using a \( 30 \times 30 \times 30 \) \( k \) mesh with Gaussians of width 0.02 Ry.

3. Results

The calculated values of the equilibrium lattice constant and bulk modulus (3.778 Å and 1.96 Mbar) are in excellent agreement with previous GGA values (3.774 Å and 2.02 Mbar)\cite{5}. However, our calculated lattice constant for this material is higher than the recent experimental value \cite{4} of 3.587 Å, but this is a usual feature of GGA calculations. The band structure for \( \text{AlCNi}_3 \) is shown in Figure 1. In this figure, the valance bands extend to about 14 eV below the Fermi level (\( E_F \) at 0 eV, shown by a broken line). The total density of states is also presented in Figure 1. There are several well defined peaks below the Fermi level. Just below the Fermi level, a peak with an energy of -0.5 eV corresponds to Ni 3d orbitals with some contributions of C 2p and Al 3p orbitals. The density of states at the Fermi level \( N(E_F) \) is calculated to be 3.02 states/eV. It is important to note that the contribution of Ni 3d states to \( N(E_F) \) is more than

\[ \text{Figure 1. } \text{The electronic band structure and total density of states for AlCNi}_3. \text{ The Fermi level corresponds to 0 eV.} \]
The vibrations of C atoms for the F$_3$ branch for AlCNi$_3$ has been made for MgCNi$_3$. The calculated phonon dispersion curves and density of states for AlCNi$_3$ using density functional linear response method.

70%. This observation clearly shows that the d bands of Ni must play a highly significant role in determining the electronic properties of AlCNi$_3$.

The energies of these phonon modes in AlCNi$_3$ are shown in Figure 2. This view is different from the phonon spectrum picture of MgCNi$_3$, for which all phonon modes are stable along the main symmetry directions [100], [110] and [111]. As the Al and Mg atoms have very similar masses, the difference in the phonon stability between these two materials can be related to the number of valence electrons: 36 for MgCNi$_3$ and 37 for AlCNi$_3$. Since the simple cubic unit cell of AlCNi$_3$ has five atoms, there are a total of 15 vibrational branches: three acoustic and twelve optical. The optical phonons at the Γ point of the Brillouin zone belong to following irreducible representations: \[ \Gamma(O_{1u}) = F_{1u}^1 + F_{1u}^2 + F_{1u}^3 + F_{2u}. \]

The energies of these phonon modes in AlCNi$_3$ are found to be 13.33 meV ($F_{2u}$), 22.03 meV ($F_{1u}$), 27 meV ($F_{1u}$) and 75.98 meV ($F_{1u}$). The $F_{1u}$ phonon mode is due to the vibrations of Al atoms. The flatness of this phonon branch along the all symmetry directions produces a very sharp peak at 27.5 meV in the phonon density of states. The lowest energy phonon mode is localised on the Ni atoms due to the heavy mass of these atoms. The $F_{1u}$ phonon mode includes atomic vibrations from all atoms in the unit cell. The energy of $F_{1u}$ mode is only 1 meV lower than the corresponding phonon mode in MgCNi$_3$. This similarity can be related to the vibrations of C atoms for the $F_{1u}$ mode.

As we have mentioned above, all phonon modes are stable along the [100] directions. Similar observations has been made for MgCNi$_3$. However, one clear difference has been found between these materials. The energy localisation of the longitudinal acoustic (LA) phonon branch along this direction for AlCNi$_3$ is different from that of MgCNi$_3$. For large $q$ wave vectors along this symmetry direction the LA phonon branch lies lower in energy than the transverse acoustic branch (TA) for AlCNi$_3$. At the zone edge point X, the eigenvector representations of phonon mode in AlCNi$_3$ are displayed in Figure 3. In this figure, electron phonon coupling parameter for these phonon modes are also presented. The lowest energy phonon mode at 5.75 meV has a longitudinal acoustic character due to vibrations of Ni atoms in [100] direction, which is parallel to $q$ wave vector direction. The TA phonon mode lies 2 meV above the LA phonon mode. The electron phonon coupling parameter for this phonon mode is around 0.38 which is far smaller than the corresponding value of 0.90 in MgCNi$_3$. However, our calculated electron phonon coupling parameter for this phonon mode is different from that of MgCNi$_3$. In addition to phonon frequencies, electron-phonon coupling parameter ($\lambda$) has been mentioned for each phonon mode.
coupling parameter for the LA phonon mode in AlCNi₃ is found to be 0.40 which is nearly two times higher than that of MgCNi₃. This can be related to the anomaly in the LA branch along the [100] direction. At the R point, TA phonon mode is stable for both materials. For AlCNi₃, electron phonon coupling parameter is calculated to be 0.60 for this phonon mode at this q point while its corresponding value is 0.99 for MgCNi₃ [2]. Our comparison for all stable phonon modes indicates that the electron-phonon coupling parameter is lower for AlCNi₃ than for MgCNi₃. The absence of superconductivity in AlCNi₃ can be related to this weak electron phonon interaction. The weak electron phonon interaction in AlCNi₃ can be related to the electronic properties of this material because the masses of Al and Mg atoms are very close to each other. Moreover, the lattice constants of these materials are different from each other only 0.8%. If there is a sharp peak close to the Fermi energy, strong electron-phonon coupling can be expected. There is a peak in the electronic density of states of MgCNi₃ [2] which lies 0.1 eV below the Fermi level. However, the nearest peak to Fermi level lies at -0.5 eV in the electronic density of states of AlCNi₃. This difference is very important because Copper pairs in the BCS theory are formed by electrons which have energies close to the Fermi energy.

4. Summary
In summary, our ab initio pseudopotential calculations using the generalised gradient approximation have produced results for the structural, electronic, and phonon properties of AlCNi₃, as well as electron phonon interaction in this material in good agreement with previously available experimental and theoretical values. Our calculations indicate that this material is a metallic. A comparison of the electronic structure of this material with that of MgCNi₃ shows that one extra valence electron in AlCNi₃ has pushed the position of the peak in the density of states just below the Fermi level to -0.5 eV, thus unfavouring formation of Cooper pairs within the context of the BCS theory of superconductivity. This conclusion is also verified from our phonon calculations. In our phonon calculations, we have observed more unstable phonon modes for AlCNi₃ than those for MgCNi₃. This difference is also due to more valence electrons in AlCNi₃ since the masses and the lattice constants of these materials are very similar to each other. However, direct electron phonon interaction calculations point out that the transverse acoustic phonon branch in AlCNi₃ has lower electron phonon coupling parameter than the corresponding branch in MgCNi₃. This clearly indicates the non existence of superconductivity in AlCNi₃.

References
[1] Shan L, Liu Z Y, Ren Z A, Che G C and When H H 2005 Phys. Rev. B 71 144516
[2] Tüütünci H M and Srivastava G P 2006 J. Phys.: Condens. Matter 18 11089
[3] Tong P, Sun Y P, Zhu X B and Song W H 2006 Phys. Rev. B 74 224416
[4] Dong A F, Che G C, Huang W W, Jia S L, Chen H and Zhao Z X 2005 Physica C 422 65
[5] Okoye C M I 2005 Solid State Commun. 136 605
[6] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[7] Vanderbilt D 1990 Phys. Rev. B 41 7892
[8] Rappe A M, Rabe K M, Kaxiras E and Joannopoulos J D 1990 Phys. Rev. B 41 1227
[9] Baroni S, Dal Corso A, de Gironcoli S and Giannozzi P http://www.pwscf.org