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Elastic properties of $MgCNi_3$—a superconducting perovskite

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Abstract

The cohesive and elastic properties of the non-oxide perovskite type superconductor $MgCNi_3$ are calculated using the full-potential linear muffin-tin orbital method with the local density approximation as well as the generalized gradient approximation for exchange and correlation. The calculated equation of state and ground state properties (equilibrium lattice constant, bulk modulus and its pressure derivative) agree well with recent experiments. From the elastic constants the Young's modulus, shear modulus, Poisson's ratio, sound velocities and Debye temperature are obtained. By analysing the ratio between bulk modulus and shear modulus we conclude that $MgCNi_3$ is intermediate between brittle and ductile in nature.

1. Introduction

The recent discovery of superconductivity in the intermetallic compound $MgCNi_3$ at temperatures close to 8 K has aroused a great deal of interest among scientists, mainly arising from the unusual characteristics of this compound [1]. Though the T_C is not particularly high, $MgCNi_3$ is peculiar in being rich in nickel, and one would expect this compound to be a strong ferromagnet rather than a superconductor. Since the discovery of superconductivity in $MgCNi_3$, there have been speculations that magnetic interactions might promote superconductivity [2], whereas specific heat measurements characterize this compound as a conventional moderate [1, 3] or strong coupling superconductor [4]. Detailed theoretical and experimental studies of the electronic structure, electron–phonon coupling and superconductivity of $MgCNi_3$ have been reported [5–10], suggesting that the superconductivity in this system is caused by the conventional phonon mechanism. Combined experimental and theoretical studies on temperature-dependent inelastic neutron-scattering measurements of the phonon density of states give evidence for a soft-mode behaviour of low-frequency Ni phonon modes [11]. A similar behaviour in the phonon spectrum of $MgCNi_3$ has also been observed recently using the pseudopotential method [12] and a lattice dynamical model theory based on pairwise interaction under the framework of the rigid ion model [13]. The

Table 1. Calculated lattice constants given in ångström, bulk modulus B_0 given in GPa and its pressure derivative B' of $MgCNi_3$ at the theoretical equilibrium volume compared with the experiment and other theoretical calculations. The bulk moduli have been calculated both at the experimental and theoretical volume ($B_0(V_0^{\text{exp}})$ and $B_0(V_0^{\text{th}})$, respectively).

	Lattice constant	$B_0(V_0^{\text{th}})$	$B_0(V_0^{\text{exp}})$	B'
LDA, this work	3.713	202.5	145.3	4.20
Other LDA	3.778[e], 3.75[h], 3.76[i], 3.74[j]	210[e], 214[f], 210[g], 202[h]		4.49[h]
GGA, this work	3.813	168.4	169.1	4.25
Other GGA	3.830[a], 3.83[d], 3.82[j]	180.5(13)[a], 172.2[d]		4.12(5)[a]
Expt.	3.810[a], 3.81[c]	—	184(5)[a], 268(7)[b], 159.6(2)[c]	2.9(5)[a], 4[b], 9.8[c]

[a] Reference [15]. [b] Reference [16]. [c] Reference [17]. [d] Reference [23]. [e] Reference [26]. [f] Reference [24]. [g] Reference [14]. [h] Reference [12]. [i] Reference [11]. [j] Reference [25].

structural stability of $MgCNi_3$ has been studied under pressure by several groups. By means of combined experiment and theory Loa *et al* studied the structural stability of $MgCNi_3$ up to a pressure of 30 GPa and concluded that the simple perovskite structure is stable in the pressure range studied [15]. The experimental zero pressure bulk modulus B_0 is reported to be 184(5) GPa with a pressure derivative $B' = 2.9(5)$. A similar high-pressure study on $MgCNi_3$ up to 22 GPa [16] reported a bulk modulus value of 268(7) GPa with $B' = 4$, while a third recent high-pressure x-ray diffraction study by Kumar *et al* [17] up to a pressure of 32 GPa reported a value of $B_0 = 156.9(2)$ GPa with a high-pressure derivative of 9.8. Hence there are significant uncertainties in the experimental compressiblity data of $MgCNi_3$.

The main focus of the present work is the elastic constants of $MgCNi_3$, which have not yet been investigated either experimentally or theoretically. The elastic constants are obtained from density functional calculations, using the local density approximation (LDA) as well as the generalized gradient approximation (GGA), of $MgCNi_3$ crystals subject to volume-conserving strains.

2. Computational details

In this work we have used the all-electron full-potential linear muffin-tin orbital (FP-LMTO) method [18] to calculate the total energies as well as the basic ground state properties. We used a double κ spdf LMTO basis (each radial function within the spheres is matched to a Hankel function in the interstitial region) for describing the valence bands. The following basis set was used in the calculations: Mg(3s, 2p, 3p, 3d), C(2s, 2p) and Ni(4s, 4p, 3d). Inside the muffin-tin spheres the charge density and potential were expanded in terms of spherical harmonics up to $l_{\text{max}} = 6$, while in the interstitial region they were expanded in plane waves, with 28 670 (energy up to 274.6 Ryd) waves being included in the expansion. The exchange correlation potential was evaluated both in the LDA [19] and in the GGA scheme [20]. Total energies were calculated as a function of volume, with 560 k-points in the irreducible wedge of the Brillouin zone, and fitted to the Birch equation of state [21] to obtain the ground state properties. The elastic constants were obtained from the variation of the total energy under volume-conserving strains, as detailed in [22].

3. Results

The calculated equilibrium lattice constant, bulk modulus and its pressure derivative are given in table 1. Both the LDA and GGA lead to a paramagnetic ground state of $MgCNi_3$, but

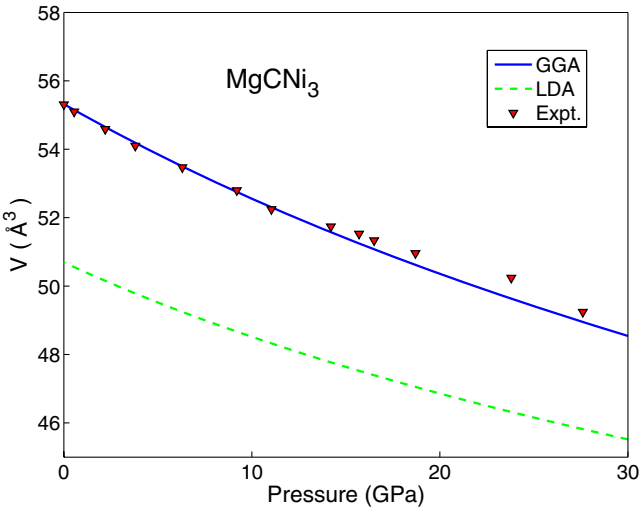

Figure 1. Calculated equation of state of $MgCNi_3$ in both the LDA and GGA approximations. Also shown are experimental data taken from [17].

(This figure is in colour only in the electronic version)

Table 2. Calculated elastic constants, shear modulus G, and Young's modulus E—all expressed in GPa—and Poisson's ratio ν of $MgCNi_3$ at the theoretical equilibrium volumes for LDA and GGA.

	C_{11}	C_{12}	C_{44}	G	E	ν
LDA	421.1	93.3	49.9	95.5	247.7	0.296
GGA	342.4	81.4	44.5	78.9	204.7	0.297

with magnetic solutions corresponding to small ferromagnetic moments on Ni quite close in energy, which indicates an irregular energy dependence on magnetism [5] and hints at large spin-fluctuations effects being present in this system. The calculated GGA lattice constant is very close to the experimental value. The bulk modulus obtained within the GGA is 9% lower than the value obtained in the experiment by [15] and 6% larger than the value obtained in [17] (the third experimental value [16] of $B = 268(7)$ GPa is significantly larger than other reported values in both theory and experiment), and also agrees well with a recent GGA full-potential linear augmented plane wave result [23]. Our LDA results agree well with the earlier published results [12, 14, 24].

The calculated GGA equation of state (EoS) is shown in figure 1, along with experimental data [17]. (The LDA equation of state is also shown, for completeness.) At the highest pressures, around 25 GPa, the GGA EoS appears slightly softer than the experimental EoS. The density of states is shown in figure 2, and is seen to be dominated by the Ni d states in the range from 0 to 4 eV below the Fermi level, with the characteristic sharp peak located around 0.1 eV below the Fermi level also reported previously [5]. Finally, the calculated cubic elastic constants of $MgCNi_3$ are given in table 2. (The values obtained in the LDA are larger than those obtained in the GGA mainly due to the smaller equilibrium volume.) In the following, we will use our calculated elastic constants to discuss the degree of ductility of $MgCNi_3$.

Pugh [28] has proposed a simple relationship, empirically linking the plastic properties of materials with their elastic moduli. The shear modulus G represents the resistance to plastic deformation, while the bulk modulus B represents the resistance to fracture. A high B/G

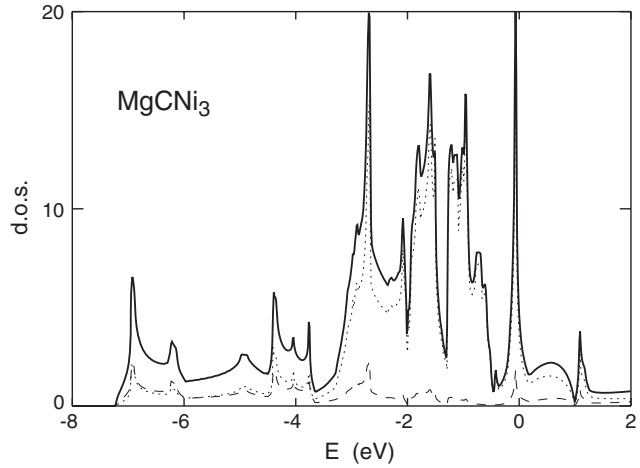

Figure 2. The density of states of $MgCNi_3$, calculated in the GGA at the experimental equilibrium constant. The full line shows the total density of states, while the dotted line shows the projection onto the Ni muffin-tin spheres and the dashed line shows the sum of the projections onto the C and Mg spheres. The energy is in electronvolts and is given relative to the Fermi level, while the density of states is in units of eV^{-1} per formula unit.

ratio may then be associated with ductility whereas a low value would correspond to a more brittle nature. The critical value which separates ductile and brittle materials is around 1.75, i.e. if $B/G > 1.75$ the material behaves in a ductile manner, otherwise the material behaves in a brittle manner. In the case of $MgCNi_3$ the value of B/G is 2.13 from our calculated values in table 2, and $MgCNi_3$ may therefore be classified as a ductile material. On the other hand, Frantsevich [29] suggested distinguishing brittleness and ductility by Poisson's ratio. According to Frantsevich the critical value of Poisson's ratio of a material is 1/3. For brittle materials such as ceramics, the Poisson's ratio is less than 1/3. Hence with ν around 0.3, the Frantsevich rule classifies $MgCNi_3$ as a brittle material, i.e. there is seemingly a contradiction between these two empirical rules for the case of $MgCNi_3$. However, it is easily shown that

$$\nu = \frac{1}{2}\frac{3\frac{B}{G} - 2}{3\frac{B}{G} + 1}, \tag{1}$$

from which it follows that Pugh's critical value corresponds to $\nu = 0.26$, so that the two empirical rules only differ on the exact border between the two types of behaviour. In view of this, $MgCNi_3$ can be considered a borderline case between the classes of ductile and brittle materials. Ductile behaviour is unusual for a perovskite material.

Pettifor [30] has suggested that the angular character of atomic bonding in metals and compounds, which also relates to the brittle or ductile characteristics, could be described by the Cauchy pressure $C_{12} - C_{44}$. For metallic bonding the Cauchy pressure is typically positive. On the other hand, for directional bonding with angular character, the Cauchy pressure is negative, with larger negative pressure representing a more directional character. These correlations have been verified for ductile materials such as Ni and Al that have a typical metallic bonding, as well as for brittle semiconductors such as Si with directional bonding [30]. Based on the calculated $C_{12} - C_{44} = 37$ GPa, we conclude that $MgCNi_3$ quite distinctly belongs to the class of metallically bonding materials, which is also what would be expected from the metallic density of states.

Table 3. Calculated longitudinal, shear and average wave velocity (v_l, v_s and v_m, respectively) in m s^{-1} and the Debye temperature θ_D in K from the average elastic wave velocity of $MgCNi_3$ at the theoretical equilibrium volume.

		v_l	v_s	v_m	θ_D
Present	LDA	7199	3874	4324	337
	GGA	6555	3521	3920	306.2
Expt.		—	—	—	292[a], 351[b], 287[c]

[a] Reference [10]. [b] Reference [27]. [c] Reference [3].

We have also derived the sound velocities and Debye temperature of $MgCNi_3$ from the calculated elastic constants [22] (see table 3). The calculated Debye temperature is in good agreement with experimental values obtained from specific heat measurements.

In summary, using first-principles density functional calculations, the mechanical properties of the non-oxide perovskite type superconductor $MgCNi_3$ have been studied for the first time. The calculated equation of state within the GGA agrees quite well with experimental data, and the elastic constants of $MgCNi_3$ have been predicted. The Debye temperature derived from the calculated elastic constants also agrees well with the experimental value. From an analysis of the elastic constants, $MgCNi_3$ is found to be intermediate between ductile and brittle with metallic bonding.

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References

[1] He T, Huang Q, Ramirez A P, Wang Y, Regan K A, Rogado N, Hayward M A, Haas M K, Slusky J S, Inumara K, Zandbergen H W, Ong N P and Cava R J 2001 *Nature* **411** 54
[2] Rosner H, Weht R, Johannes M D, Pickett W E and Tosatti E 2002 *Phys. Rev. Lett.* **88** 027001
[3] Lin J-Y, Ho P L, Huang H L, Lin P H, Zhang Y-L, Yu R-C, Jin C-Q and Yang H D 2003 *Phys. Rev.* B **67** 052501
[4] Mao Z Q, Rosario M M, Nelson K D, Wu K, Deac I G, Schiffer P, Liu Y, He T, Regan K A and Cava R J 2003 *Phys. Rev.* B **67** 094502
[5] Singh D J and Mazin I I 2001 *Phys. Rev.* B **64** 140507(R)
[6] Shim J H, Kwon S K and Min B I 2001 *Phys. Rev.* B **64** 180510(R)
[7] Dugdale S B and Jarlborg T 2001 *Phys. Rev.* B **64** 100508(R)
[8] Shein I R, Ivanovskii A L and Medvedeva N I 2001 *JETP Lett.* **74** 122
[9] Ignatov A Yu, Savrasov S Y and Tyson T A 2003 *Phys. Rev.* B **68** 220504(R)
[10] Wälte A, Fuchs G, Müller K-H, Handstein A, Nenkov K, Narozhnyi V N, Drechsler S-L, Shulga S, Schulty L and Rosner H 2004 *Phys. Rev.* B **70** 174503
[11] Heid R, Renker B, Schober H, Adelmann P, Ernst D and Bohnen K-P 2004 *Phys. Rev.* B **69** 092511
[12] Tütüncü H M and Srivastava G P 2006 *J. Phys.: Condens. Matter* **18** 11089
[13] Jha P K 2005 *Phys. Rev.* B **72** 214502
[14] Kumary T G, Janaki J, Mani A, Jaya S M, Sastry V S, Hariharan Y, Radhakrishnan T S and Valsakumar M C 2002 *Phys. Rev.* B **66** 064510
[15] Loa I, Syassen K, Hanfland M, Zhang Y L, Yu R C and Jin C-Q 2002 Internal Report, MPI/FKF, Stuttgart (see poster under http://www.fkf.mpg.de/hd/)
[16] Youlin Z, Fengying L, Liangchen C, Jing L, Richeng Y, Zhenxing L, Wen Y and Changqing J 2003 *Chin. Sci. Bull.* **48** 2287

[17] Kumar R S, Cornelius A L, Shen Y, Kumary T G, Janaki J, Valsakumar M C and Nicol M F 2005 *Physica* B **363** 190
[18] Savrasov S Y 1996 *Phys. Rev.* B **54** 16470
[19] Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
[20] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[21] Birch F 1938 *J. Appl. Phys.* **9** 279
[22] Kanchana V, Vaitheeswaran G, Svane A and Delin A 2006 *J. Phys.: Condens. Matter* **18** 9615
[23] Okoye C M I 2003 *J. Phys.: Condens. Matter* **15** 833
[24] Johannes M D and Pickett W E 2004 *Phys. Rev.* B **70** 060507(R)
[25] Sieberer M, Mohn P and Redinger J 2007 *Phys. Rev.* B **75** 024431
[26] Haze I 2004 *Phys. Rev.* B **70** 033105
[27] Shan L, Xia K, Liu Z Y, Wen H H, Ren Z A, Che G C and Zhao Z X 2003 *Phys. Rev.* B **68** 024523
[28] Pugh S F 1954 *Phil. Mag.* **45** 823
[29] Frantsevich I N, Voronov F F and Bokuta S A 1983 *Elastic Constants and Elastic Moduli of Metals and Insulators Handbook* ed I N Frantsevich (Kiev: Naukova Dumka) pp 60–180
[30] Pettifor D 1992 *Mater. Sci. Technol.* **8** 345