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The elastic and thermodynamic properties of new antiperovskite-type superconductor $CuNNi_3$ under pressure

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ABSTRACT

The crystal structural, elastic and thermodynamic properties of antiperovskite-type superconductor $CuNNi_3$ under pressure are investigated by using the density functional theory within the generalized gradient approximation (GGA). The ground-state properties are found to agree with the available experimental data and others theoretical results. The elastic constants, shear modulus and Young's modulus, Debye temperature, melting point and minimum thermal conductivity under pressure are calculated, the results show those properties increase monotonically with increasing pressure. Finally, the ductility of $CuNNi_3$ was analyzed using the B/G ratio, Cauchy pressure and Poisson's ratio σ.

1. Introduction

Since the discovery of the new intermetallic non-oxide antiperovskite superconductor $MgCNi_3$ by He et al. [1], many scientists pay more attention to find new superconductor among the antiperovskite compounds $MCNi_3$ [2–9], where M is a group II or III element. Recently, A set of antiperovskite-type Ni-rich nitrides $MNNi_3$ (M=Zn, Mg, Cd, Sn and In) had been synthesized [10–14]. Bannikov et al. [15] systematically investigated the elastic properties of 12 synthesized and hypothetical cubic antiperovskite-type Ni-rich nitrides $MNNi_3$ (M=Zn, Cd, Mg, Al, Ga, In, Sn, Sb, Pd, Cu, Ag and Pt) by ab initio calculations. Very recently, a new type of Ni-based nitrogen containing superconductor $CuNNi_3$ (Cu: cube-corner position; N: body-center position; Ni: face-center position) and with the superconducting transition temperature $T_c=3.2$ K has been synthesized by solid-gas reactions of Cu and Ni metal powder in NH_3 gas and some of its properties had been investigated [16]. There are some evidences suggesting that $CuNNi_3$ may represent a new type of unconventional superconductivity and many fundamental questions about the nature of its superconducting state still remain unanswered.

Up to now, however, there have not been detailed studies for the elastic and thermodynamic properties of $CuNNi_3$ under pressure. In view of these circumstances, we calculated the crystal structural, elastic and thermodynamic properties of $CuNNi_3$ under pressure by using the first-principle in order to understand its peculiarity physical properties. The rest of the paper is organized as follow: in Section 2, we describe briefly the computational techniques used in this work; Section 3 contains our results and discussion, involving structural and elastic properties, and some thermodynamic properties such as melting point, minimum thermal conductivity and Debye temperature for the $CuNNi_3$ under pressure; Finally, the conclusion is given in Section 4.

2. Calculation methods

Our first-principle calculations were performed using the CASTEP code, which is based on the framework of the

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density functional theory (DFT) using the ultra-soft pseudo-potential plane-wave (UPPW) method. For the exchange and correlation terms, the Perdew–Burke–Ernzerhof (PBE) [17] function was used within the generalized gradient approximation (GGA). Using the UPPW method, $2s^2 2p^3$ of N, $3d^8 4s^2$ of Ni and $3d^{10} 4s^1$ of Cu were treated explicitly as valence electrons. Cutoff energy of plane-wave is 650 eV and a $10 \times 10 \times 10$ Monkhorst–Pack k-point mesh has been employed in this study because it gives a sufficiently accurate energy of $CuNNi_3$. The structural parameters of $CuNNi_3$ were calculated by using the Brodyden–Fletcher–Goldfarb–Shanno (BFGS) [18–21] method, with the threshold for converged structures: energy change of per atom less than 5×10^{-6} eV/atom, the Hellmann–Feynman force of per atom less than 0.01 eV/Å and the maximum displacement of atom is 5×10^{-4} Å during the geometry optimization.

3. Results and discussions

3.1. Volume and lattice parameters change

To investigate ground-state properties, the equilibrium lattice constant of $CuNNi_3$ was computed first. The optimized lattice constant and elastic constants of $CuNNi_3$ are summarized in Table 1, including experimental data by other scholars for comparison. Our calculated value of the lattice constant is 3.761 Å, which is very close to the experimental value 3.742 Å [16]. The difference between the experimental and the calculated value is 0.5%. The reasons why there is a difference between theoretical values and experimental data are as follow: the theoretical values gained by GGA approximation method are often higher than experimental data. These results show and confirm that the method used in this study is reliable thereby the optimized lattice constants can be used for future calculations of other parameters.

In order to show how the structural parameters under pressures in this compound behave, the equilibrium geometries of $CuNNi_3$ unit cell were computed at fixed values of applied hydrostatic pressure in the range from 0 to 20 GPa with each step of 4 GPa, with a complete optimization for the structural parameters performed at each pressure. Fig. 1 plots the variation of the relative changes of the lattice parameters (a/a_0 and V/V_0) versus applied hydrostatic pressure (P). The following relations can be

Table 1
Structural parameters of $CuNNi_3$ at zero-pressure: lattice constants a_0, bulk modulus B_0, and its pressure derivative B_0' along with available calculated results.

	a_0 (Å)	B_0 (GPa)	B_0'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
Our work	3.761	201.7*	4.77	333.4	9.7	124.8
Ref [10]	3.761	201.8	4.40**[2]	349.2	32.6	128.2
Ref [15]	3.745	213.6	−/−	396.9	7.8	121.9

* B_0 calculated by third-order Birch–Murnaghan equation.
** B_0' the value of $MgNNi_3$.

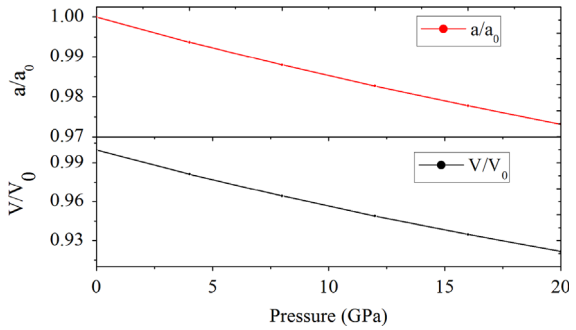

Fig. 1. (a) Lattice constant-pressure relation, the solid line is a quadratic least-square fit. (b) Volume–pressure relation, the solid line is given by EOS.

obtained from this calculation.

$$a/a_0 = 0.99996 - 0.00161P + 1.33929 \times 10^{-5} P^2 \quad (1)$$

The calculated unit cell volumes at fixed values of applied hydrostatic pressure in the range from 0 to 20 GPa were used to construct the equation of state (EOS), which was fitted to a third-order Birch–Murnaghan equation [22]:

$$P = \frac{3}{2} B_0 \left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3} \right] \left[1 + \frac{3}{4}(B' - 4) \left\{ \left(\frac{V_0}{V}\right)^{2/3} - 1 \right\} \right] \quad (2)$$

The fixed value of V_0 is determined by the zero-pressure data. The calculated values of the bulk modulus B_0 and its pressure derivative B_0' at zero pressure are listed in Table 1. The calculated B_0 of $CuNNi_3$ matches well with the results reported in previous theory work. From Table 1 we can see that the calculated value of B_0 from the elastic constants has nearly the same values as the one obtained from the EOS fitting, this might be an estimate of the reliability and accuracy of our calculated elastic constants of $CuNNi_3$.

3.2. Elastic behavior under pressure

Elastic constants of crystals provide a link between mechanical and dynamical behaviors. Also, they give important information concerning the elastic response of a crystal to an external pressure. To calculate the elastic constants, we have applied the volume-conserving method. In this way the values of three independent elastic constants in the cubic symmetry are estimated.

In Fig. 2, we present the variation of the elastic constants and the elastic modulus of $CuNNi_3$ under pressure. We clearly observe that the elastic constants C_{11}, C_{12}, C_{44}, elastic modulus B, shear modulus G and Young modulus E increase monotonically with increasing pressure. In Fig. 2, we also can see that the values of C_{11} are very large among elastic constants, which indicate that it is very incompressible under uniaxial stress along x axis. The pressure derivatives are listed in Table 2. It is clear that the C_{11} and B are more sensitive to the change of pressure compared to the other modulus. The atoms are closer under high pressure, and then the electrostatic repulsive force increases. So it is difficult for the atoms to move and the hardness is increased.