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Predicting the Debye Energy and Temperature of XB_2 (X=Mg and Ca) Hexagonal Superconductors at 0K

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Abstract

We present detail results of the Debye temperature, Debye Vibrational energy, and Debye heat capacity of Hexagonal XB_2 Superconductor material at 0K using SISSA (Scuol International Superiore di Studi Avanzati) with calculation by thermo_pw on density functional theory(DFT) within Generalised Gradients Approximation (GGA) that is used to describe exchange-correlation potential with Perdew, Burk and Ernzenhof (PBE) flavour at 0K. The calculation of the Debye temperature of MgB_2 and CaB_2 at 0K are in agreement with some theoretical data obtained at a higher temperature. The results calculated indicated that Debye temperature of MgB_2 is much higher than CaB_2, with MgB_2 more strongly bonded, stiffens and harder than CaB_2. But CaB_2 with less Debye temperature are weakly bonded with less stiffness. An attempt was made to calculate Debye Vibrational energy, and Debye heat capacity all at 0k with different values showed that their results are not found in the literature. These superconductors are desirable materials for manufacturing of electric cables and magnetic resonance imaging(MRI).

Keywords: First principle; Debye vibrational energy and Debye temperature; Hexagonal superconductor; Diboride.

1. INTRODUCTION

In investigating the Debye model as a method for estimating the phonon contribution to the thermodynamic properties of a solid state. It treats the vibrations of the atomic heat as phonons in a box. Hence, it predicts the value of low-temperature dependence for heat capacity which is proportional to T^3, i.e., Debye T^3, with Dulong-Pett Law at high temperature, due to assumptions, the accuracy suffers at the intermediate temperature. However the value of Debye temperature is related to either elastic constant or specific heat thermal expansion measurements, Furthermore, this can also be achieved by using thermo_pw to determine the Debye temperature, Debye Vibrational free energy, Debye Entropy and Debye heat capacity setting the temperature to 0k, the highest temperature can be achieved due to a single normal vibration [1]. The value of the Debye temperature for superconducting and Normal from low and high-temperature superconductors with high Debye temperature can also be obtained [2][3]. The Debye model can be used with the wide spectrum of frequencies to describe the complicated pattern of lattice vibrations. This is assumed that the hypothetical oscillators generate pure sine waves throughout the crystals and these will have displaced the atoms away from the equilibrium position by an equal amount to the amplitude of sine wave at the point. The distribution of the oscillators is quasi-continuous in hence integration can be used instead of summation [4].

Here, in this paper, we present the data obtained for Debye temperature using thermo_pw for the Hexagonal XB_2 materials at 0k, also Debye Vibrational energy and Debye heat capacity all at 0k.

The hypothetical binary superconductors XB_2.i.e MgB_2, CaB_2 and AgB_2 will have improved and desirable properties. These desirable properties can be obtained by tunning of Debye temperature, Debye vibrational energy and Debye heat capacity up to production production of electric cable and Magnetic Resonance Imaging(MRI) .The main purpose of this study is to provide first-principles calculation of Debye temperature, Debye vibrational energy and Debye heat capacity of MgB_2,CaB_2 and AgB_2 with thermo_pw.The remaining parts of the work are organized in the following ways: Section 2 gives the computational methods, while the main results and discussion are given in Section 3. Finally, conclusion are stated in Section 4.

2. CALCULATION DETAILS

(a) Computational Parameters

The Debye temperature, Debye Vibrational energy, Debye Vibrational free energy, Debye Entropy and Debye heat were obtained by SISSA (Scuol International Superiore di Studi Avanzati) with the calculation by thermo_pw to produce the input file for the pw.x of QUANTUM ESPRESSO that implements density functional theory(DFT)[5]-[9] within Generalised Gradients Approximation (GGA). The inputs files used with five information: The Bravis lattice, the position of the atoms inside the unit cell, the type of atoms and pseudopotentials files that will be used for the cut-off energies. The pseudopotential was generated by atom program as included in

SISSA in accordance to Troullier and Martins scheme [10] using with GGA by Perdew, Burk and Ernzerhof(PBE)[11] exchange and correlation potential and 'atomic' code [12]. The transferability of pseudopotentials of Mg, Ca and B was tested by reproducing corresponding bulk properties.

For angular frequency

For 3D states with the volume of sphere V and number of states of degeneracy states as

Since Sound propagate with two transverse waves and one longitudinal wave in a solid.

Therefore total number of states = $3g(\omega)d\omega$

Total energy of the system=phonon x Average no of x No of mode

Energy phonon

Where Phonon energy=, Average number of phonons = $\dfrac{1}{\exp\left(\dfrac{\hbar\omega}{K_B T}\right)-1}$

No of modes=

Now

$$E = \frac{3V}{2\pi^2 v^3}\int_0^{\omega_{\max}} \frac{\hbar\omega^3}{\exp\left(\dfrac{\hbar\omega}{K_B T}\right)-1} d\omega \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Let $x = \dfrac{\hbar\omega}{K_B T}$ and Debye Temperature: $\theta = \dfrac{\hbar\omega_{\max}}{K_B}$

Equation (2) will now be express as

$$E = \frac{3VK_B T^4}{2\pi^2 v^3 \hbar^3}\int_0^{\theta_D/T} \frac{x^3}{\exp(x)-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Equation (3) define Debye model heat energy

At Low temperature

Take limit and use identity $\int_0^\infty \frac{x^3}{\exp(x)-1}dx = \frac{\pi^4}{15}$

So

Therefore, Debye heat capacity is defined as

$$C = \frac{dE}{dT} = \frac{12\pi^4}{5} NK_B \left(\frac{T}{\theta_D}\right)^3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

In equation (5) it showed the Debye T^3 law.

At high Temperature

X is small

Therefore $\exp(X) \approx 1 + X$........So

$$\int_0^{\theta_D/T} \frac{x^3}{(1+x+\ldots)-1}dx \approx \frac{\theta_D}{3T^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$E = \frac{VK_B^4 T\theta_D^3}{2\pi^2 v^3 \hbar^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

And Since $v = \frac{\theta_D K_B}{\hbar}\left(6\pi^2 \frac{N}{V}\right)^{-1/3}$

$$E = 3NK_B T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Debye heat capacity

$$C = \frac{dE}{dT} = 3NK_B \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Equation (5) is the specific heat capacity of Debye model at low temperature and equation (9) is the Debye specific heat capacity at high temperature. Hence equation (10) implies Dulong-Petit

3. RESULTS AND DISCUSSION

Table 1: Debye Temperature AIB_2-type Superconductors

Method	*DEBYE TEMPERATURE $\Theta_D(K)$*
MgB_2 Present Work	1020.203[a]
Exp.	750.30[b],746[d],800[e].
Theory	1016.60[c]
CaB_2 Present	874.663[a]
Exp.	-
Theory	894.60[c]

[a]Present result

[b]Re[13]

[c]Ref[14]

[d]Ref[15]

[e] Ref [16]

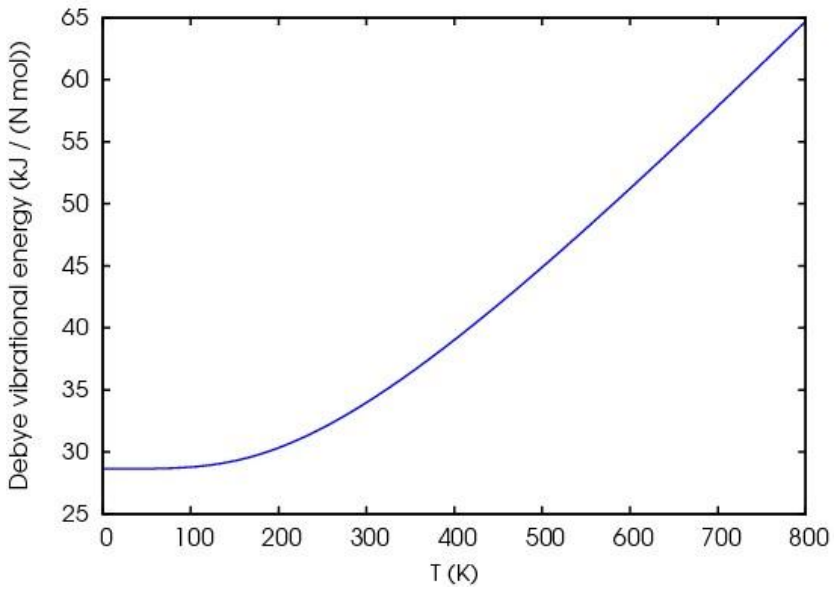

Figure 1: Debye vibrational energy (KJ/(Nmol)) at different temperatures T(K) of MgB_2

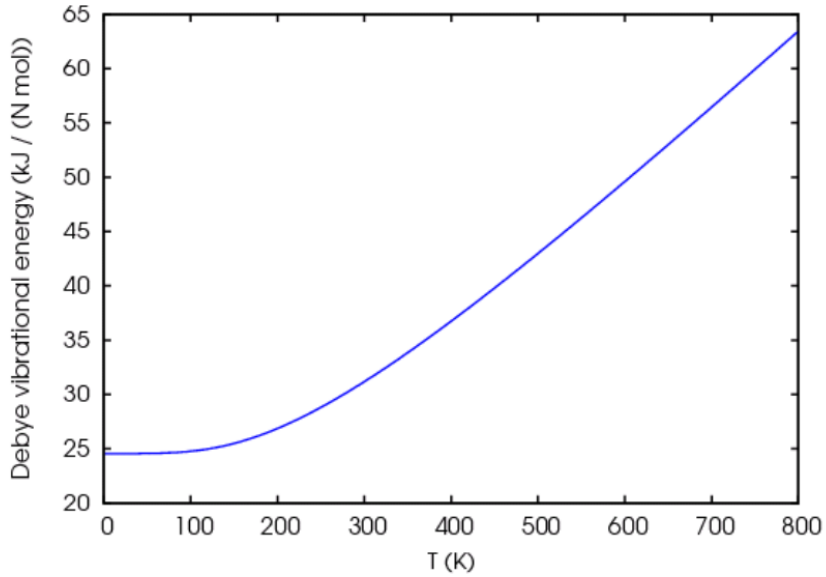

Figure 2: Debye vibrational energy (KJ/(Nmol)) at different temperatures T(K) of CaB_2

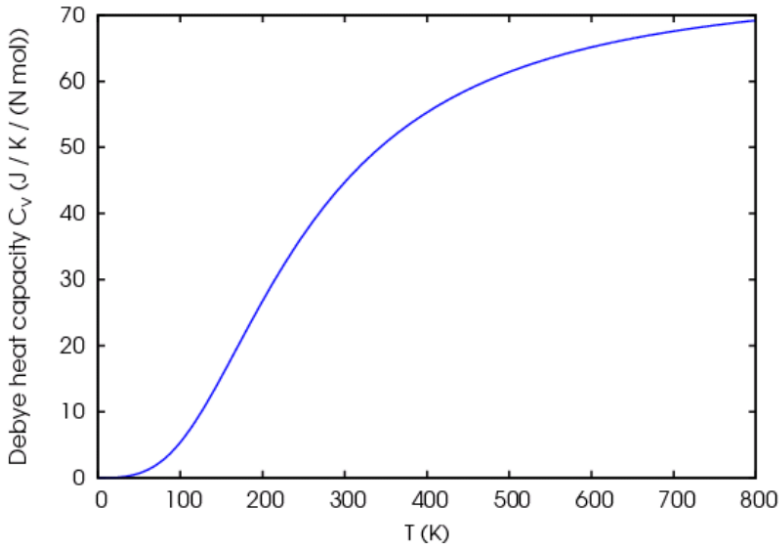

Figure 3: Debye heat capacity C*v* (J/K/(Nmol)) at different temperatures T(K) of MgB

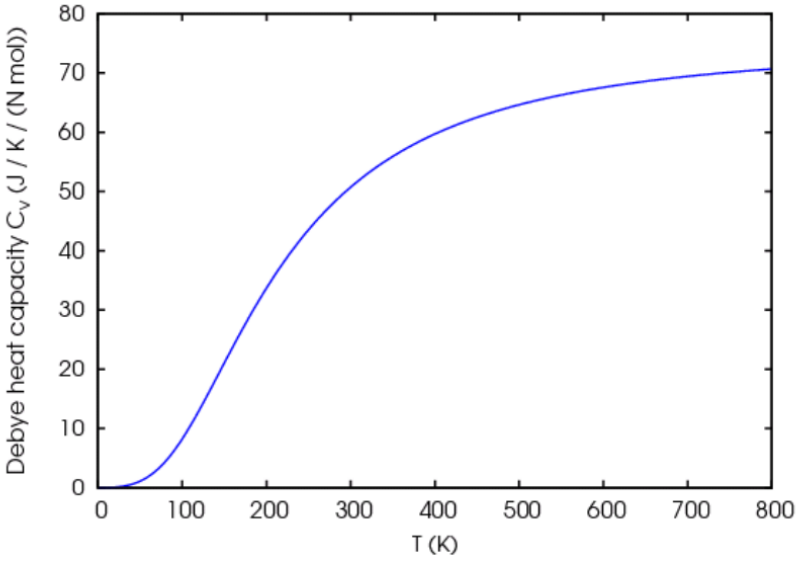

Figure 4: Debye heat capacity C*v* (J/K/(Nmol)) at different temperatures T(K) of CaB_2

Thermodynamic properties of hexagonal XB_2 –type superconductors were investigated in MgB_2, CaB_2 and AgB_2 by using harmonic Debye model. The used method is as: the geometric optimization of those superconductors were performed using ab-initio thermo_pw based on Density Functional Theory (DFT) within the Generalised Gradient Approximation(GGA) of Perdew-Burke-Eruzerhof (PBE) is also used for the exchange and correlation terms.

From Table1, the Debye temperature of hexagonal AIB_2-type superconductor of MgB_2, CaB_2 and AgB_2 were presented as obtained from thermo_pw measurements. For MgB_2, the present calculated result of Debye temperature is larger than the experimental results by the estimated range of 10-20% [13][14][15] while the theoretical calculated value are close to the estimation of 0.4%[8] which are in agreement with the present result. For CaB_2, the present calculated result of Debye temperature showed that its slightly less than the theoretical value by estimation of 0.34%[16]. Moreover, these result shows that the calculated Debye temperature for MgB_2 crystal much higher which indicated that Dulong-Petit is a poor fit at room temperature and strongly bonded while CaB_2 crystals have high Debye temperature which stated that Dulong-Petit reasonable fit at room temperature and strong bounded. Also the result stated that MgB_2 crystal much stiffness and harder than CaB_2 crystal. For example, Diamond is 224K, much higher than 402K of graphite [17]. These results are in agreement with the reported theoretical values.

The thermodynamic properties of XB_2 hexagonal structures are calculated in the temperature range from 0 to 800K, where the quasi-harmonic Debye model remains fully applicable. We see from Figure 1 and Figure 2 shows Debye vibrational energy in variation with the temperature at constant volume for XB_2 structure in MgB_2 and CaB_2. By using thermo_pw which are obtained from first-principles calculation of the constant amount to T=0K, the Debye vibrational energy at constant volume for MgB_2 and CaB_2 are 29KJ/(Nmol) and 24.5KJ/(Nmol) respectively. As the Debye vibrational energy increases with increase in the temperature and the shape of curve is nearly linear for both of the phases at T=8000K the Debye vibrational energy for in MgB_2, CaB_2 and AgB_2 are 64.5KJ/(Nmol) and 64KJ/(Nmol) respectively, but there is no experimental and theoretical data found in literature.

The Debye specific heat capacity varies with the temperature at constant volume are shown in Figure 3 and Figure 4. For MgB_2 as in Figure 3 at T<100K low-temperature limit C_v occur but the temperature increases from 100-800K with Debye temperature. In this two cases, both phonon approach and Debye model result in almost the same prediction of Debye heat capacity. The calculated result with the experimental data down to room temperature are not found in literature. For CaB_2 in Figure 4 have similar behaviour as in MgB_2 but with the difference in at lower temperature 100K the Debye specific heat capacity is 8(J/K/(Nmol)) while at 800K for a higher limit Debye specific heat capacity is 70(J/K/(Nmol). In this case, no experimental data found in the literature.

It can be seen that Debye heat capacity C_v increases with increase in temperature. These results indicate that phonon thermal soften occurs when the temperature was raised. In lower temperature limit C_v T<100K obeys the expected law of Debye T^3 power law behaviour, at high-temperature T it follows that the Dulong and Petit law and C_v increase monotonically by approaches the classical limit C_v=3NK where R=NK, Hence Cv=3R.

4. **CONCLUSION**

To investigate, prediction of Debye energy and Debye temperature, we use SISSA with the calculation by thermo_pw to produce the input file for the pw.x of QUANTUM ESPRESSO that implements density functional theory(DFT) within local density approximation (LDA) and Generalised gradients approximation (GGA) at 0K. The Debye temperature, Debye Vibrational energy and Debye heat capacity were studied fruitfully using the Debye quasi-harmonic Debye model, and the results were discussed. The Debye temperature of MgB_2 is much higher than that of CaB_2, this indicates that of MgB_2 are firmly bonded, much stiffness and hardness than CaB_2. Also, Debye vibrational energy and Debye specific heat capacity were obtained from thermo_pw. These results obtained from these workers were not found in experimental and theoretical in literature. Moreso, the work has predicted that the Debye energies and Debye temperature results could be calculated at 0K.

REFERENCES

[1] S.Baroni , S. de Gironcoll, A. Dal Corso, Giannozzi, P .*Rev.Mod.Phys*.73(2011).515-562

[2] B.S. Chndrasekhar and J.A Rayne *Phys.Rev.Lett*. 6.(1961) .3

[3] J.Klen, A.Ledger, S.de chevigne, D. MacBride, M.Belin and D.Defournea. *Solid state communication* .Vol 33(1980) issue 11.

[4] Charles Kittel, *Solid state Physics*, 1976, John Wiley and Sons.Inc.

[5] P.Hohenberg, W.Kohn. Phys.Rev.B 136 (1964) 864.

[6] W.Kohn, L.J.Sham.Phys.Rev.A 140 (1964) 1133.

[7] J.P. Walter and M.L.Cohen, Phys.Rev.B 4 (1971) 1877.

[8] R.Car and M.Parrinello. Phys.Rev.Lett. 55 (1985) 2471.

[9] R.M.Dreizler and E.K.U.Gross, in Density Functional Theory,Springer-Verlag Berlin Heidelberg (1980).

[10] N.Troullier, J.L.Martins. Phys.Rev.B.43 (1991) 1993.

[11] J.P Perdew, k.Burk,M. Ernzerhof, *Phys.Rev.Lett*.77(1996) 3865.

[12] A.D .Corso, Pseudopotential generation and test *by IdI,x* atomic code

[13] S.L. Bud'ko,G.L Lapertot, C.E.Cunnlgham ,N. Anderson and P.C.Canfield. *Phys,Rev.Lett* .86(2001),No.1, pp.1877.

[14] P.Ravindran, L.Past, P.A Fast, P.A. Korzhavi, B.J. Johnson. *J.Appl.Phys*. 84(1998).4891-4904

[15] Y.Wang, T.Packoushi and A.Junod. *Physica.C:Superconductivity* and its applications.355(2001),179-193.

[16] K.Kremer, B.J.Gibson. and K.Ahn .2001.*Cond-mat/0103319*.

[17] T. Tohei, A.Kuwabara, F.Oba and I.Tanaka . *Phys.Rev.B.*73(2006).064304.

[18] We used the pseudopotential Mg.pbe-n-kjpaw. UPF http://qe-forge.org/project/pslibrary/

[19] We used the pseudopotential Ca.pbe-spn-kjpaw. UPF http://qe-forge.org/project/pslibrary/

[20] We use the pseudopotential B.pbe-dn-kjpaw. UPF http://qe-forge.org/project/pslibrary/