



Phonon properties of intrinsic insulating phase of the cobalt oxide superconductor NaCoO_2

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Abstract

We report a systematic and detailed lattice dynamical investigation on the intrinsic insulating phase of the cobalt oxide superconductor NaCoO_2 . The phonon dispersion curves, partial and total phonon densities of states are obtained. The calculated Raman, infrared phonon modes and generalized phonon density of states agree reasonably well with the experimental spectra. These studies have enabled an atomic level understanding of the phonon density of states. The effect of Na site occupancy on the phonon spectra are discussed and found significant differences. The lattice specific heat at constant volume and Debye temperature are also reported. The estimated Debye temperature reveals the importance of phonons in the transport properties in the intrinsic insulating phase of the NaCoO_2 compound at room temperature. The temperature dependence of the vibrational amplitudes has also been discussed.

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1. Introduction

In recent years cobalt oxide systems have been studied intensively because of their wide range of unique and interesting magnetic [1,2] and thermoelectric [3] properties as well as for possible analogies to colossal magnetoresistive manganite

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materials or high transition temperature superconducting cuprate oxides. Thereafter, the recent discovery of superconductivity in water-intercalated Na_xCoO_2 compound ($\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$) which is a breakthrough in the search for new layered transition metal oxide superconductors immediately spurred tremendous round of intense interest in this system [4,5]. Although the superconducting transition temperature $T_c \approx 5\text{ K}$ is much lower than T_c 's in cuprate superconductor, both systems share many common features. Similar to cuprates the Co-based superconductor represents a strongly correlated and anisotropic type II system [6–9]. As far as superconducting mechanism in this compound is concerned, a large number of experimental investigations suggest that the superconductivity in this material is unconventional [6,10,11]. To understand the mechanism of superconductivity in this material some theoretical models such as resonating valence bond [12–15] and spin triplet superconductivity [16–19] have been proposed. But, these theoretical investigations do not lead to any firm conclusions as far as mechanism of superconductivity in this material is concerned. However, some experiments suggest the presence of strong electron–phonon coupling in this compound [20–22]. Therefore, it is a right juncture to investigate the phonon properties of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ and its parent compound. A detailed understanding of the lattice vibrations is in view of the possible role of phonons in the superconductivity and in the understanding of the physical nature of the interatomic forces in these compounds.

As far as the investigations of detailed and systematic phonon properties for these compounds are concerned very few attempts have been made so far. While there are some Raman [23,24], infrared [20,25] and neutron scattering [26,27] experiments on the investigations of the lattice dynamical properties of these compounds very scant attention has been so far paid toward the theoretical investigations [27,28] on these properties. Very recently Li et al. [28] have performed the lattice dynamical calculations for parent NaCoO_2 compound by using first principles method. In this study they report the phonon frequencies throughout the Brillouin zone and phonon density of

states. However, the results of the first principles calculation of Li et al. [28] are in general good agreement with the experimentally investigated Raman and infrared phonon modes but failed in predicting the experimental phonon density of states (DOS) obtained by using inelastic neutron scattering [27]. While the measured spectra reports phonon density up to 100 meV ($\approx 800\text{ cm}^{-1}$), the phonon DOS calculated by using first principles report the phonon density only upto 80 meV ($\approx 600\text{ cm}^{-1}$). Also, there is contradiction on the sensitive phonon modes to the Na site occupancy with the shell model results of Lemmens et al. [24]. The results of the shell model calculation of Lemmens et al. [24] are only reported for Raman modes and hence a detailed and systematic lattice dynamical calculation for NaCoO_2 compound is necessary. It is indeed essential to find out that if the present simple model based on interatomic interaction with more realistic and physical parameters is sufficient to describe the vibrational properties of the phonon properties of intrinsic insulating phase of the cobalt oxide superconductor NaCoO_2 .

In the present article, we report a systematic and detailed investigation on the phonon properties of the intrinsic insulating phase of the cobalt oxide superconductor NaCoO_2 by using a simple lattice dynamical model theory based on interatomic potential approach. The phonon properties for NaCoO_2 investigated in the present study are the zone center phonon modes, phonon dispersion curves, phonon density of states and thermal properties. The paper is organized as follows: in Section 2, we briefly describe the theoretical lattice dynamical model. In Section 3, we present Results and discussion, followed by Conclusions in Section 4.

2. Theoretical model and method of calculation

For ionic materials, interatomic potential in the form of a Buckingham potential is rather a traditional model, which has been shown to perform sufficiently well and, therefore, it is widely used for modeling various oxides. This potential

takes the form

$$U_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + b_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right), \quad (1)$$

where the first and second term represent the Coulomb potential and Born–Mayer repulsion energies, respectively. Here, r_{ij} is the interatomic distance between atoms i and j , Z_i and Z_j are the

Table 1
The parameters of the potential

Interactions	Short-range interactions		Effective charge	
	b_{ij} (eV)	ρ_{ij} (Å)	Ion	Z
Na–O	1025.4	0.3734	Na	1.67
Co–O	1341.4	0.3214	Co	2.13
O–O	22764.00	0.1490	O	–1.90
Ion		Y (e)		K (eV–Å ²)
Shell model ^a O ^{2–}		–2. 86902		74.92

^a Y and K refer to the shell charge and harmonic spring constant respectively.

Table 2
Zone center optical phonon modes of NaCoO₂. All frequencies are in cm^{–1}

Modes	Present calculation		Others
	Geometry A	Geometry B	
Raman active modes			
A _{1g}	586.66	597.92	608.0 ^a , 604.6 ^b , 574 ^c , 598 ^d , 582 ^e , 588 ^f
E _{1g}	492.00	504.12	477.1 ^a , 482.1 ^b , 458 ^c , 480 ^d , 469 ^e
E _{2g}	177.13	194.99	172.9 ^a , 185.7 ^b
E _{2g}	496.10	515.10	483.7 ^a , 489.8 ^b , 494 ^c
Infrared active modes			
E _{1u}	204.70	218.12	201.2 ^a , 216.5 ^b
E _{1u}	602.57	610.00	586.7 ^a , 590.0 ^b , 570 ^e , (505,530,560,575) ^h
A _{2u}	353.48	333.94	397.5 ^a , 337.0 ^b
A _{2u}	575.34	566.11	569.8 ^a , 566.5 ^b
Silent modes			
B _{1g}	315.97	302.60	351.7 ^a , 309.9 ^b
B _{1g}	602.79	613.40	622.4 ^a , 616.0 ^b
B _{2u}	168.79	160.03	197.0 ^a , 172.1 ^b
B _{2u}	598.20	610.23	616.2 ^a , 610.0 ^b
E _{2u}	87.50	92.51	88.0 ^a , 95.2 ^b
E _{2u}	575.6	585.10	582.8 ^a , 585.6 ^b

^a Ist principles calculation [28] of NaCoO₂ in their geometry A.

^b Ist principles calculation [28] of NaCoO₂ in their geometry B.

^c Raman frequency [23] of Na_{0.7}CoO₂.

^d Raman frequency [24] of Na_xCoO₂ · y H₂O.

^e Raman frequency [24] of Na_{0.3}CoO₂ · 1.3H₂O.

^f Raman frequency [24] of Na_{0.7}CoO₂ single crystal.

^g Infrared frequency [20] of Na_{0.57}CoO₂.

^h Infrared frequency [25] of Na_{0.7}CoO₂.

effective charges of the respective atoms, b_{ij} and ρ_{ij} are the short-range potential parameters for each pair of atoms usually found by fitting to experimental data. For the potentials described, O–O short-range interactions were chosen from Ref. [29], which were successfully used for the modeling of oxides [30,31]. The electronic polarization of the lattice is included by the shell model. In this model, an ion is represented by a massless shell of charge Y and a core of charge X which are coupled by a harmonic spring constant K . To calculate the phonon properties the software LADY for lattice dynamical simulation is used [32]. We have only considered the oxygen ions polarizable. The parameters so obtained are listed in Table 1.

3. Results and discussion

3.1. Zone center phonon frequencies

For the present calculations of the phonon properties, we have considered the intrinsic NaCoO₂ having a hexagonal structure (space group # 194, P6₃/mmc) with lattice constants of $a = 2.82 \text{ \AA}$, $c = 10.92 \text{ \AA}$ and the structural parameters Co at 2a (0,0,0); O at 4f (1/3,2/3,z); Na1 at 2d (2/3,1/3,1/4) and Na2 at 2b (0,0,1/4) [23]. A symmetry analysis taking into account the P6₃/mmc point group for NaCoO₂ leads to the following zone center phonon modes

$$\Gamma(\text{P6}_3/\text{mmc}) = A_{1g} + 2B_{1g} + E_{1g} + 2E_{2g} + 3A_{2u} + 2B_{2u} + 3E_{1u} + 2E_{2u}, \quad (2)$$

where the $A_{1g} + E_{1g} + 2E_{2g}$ modes are Raman active and $3A_{2u} + 3E_{1u}$ modes are infrared active. Each of the E_{2g} and E_{1u} modes is doubly degenerate. The B_{1g} , B_{2u} and E_{2u} are silent modes. The Raman active modes A_{1g} and E_{1g} involve vibrations from oxygen atoms only while E_{2g} modes are related to Na and oxygen. Due to full point group symmetry the Co sites do not contribute to the Raman scattering. The calculated frequencies of the phonon modes at zone center in two geometries are presented in Table 2 along with the other available calculated and experimental values. As can be seen from the Table 2 that the

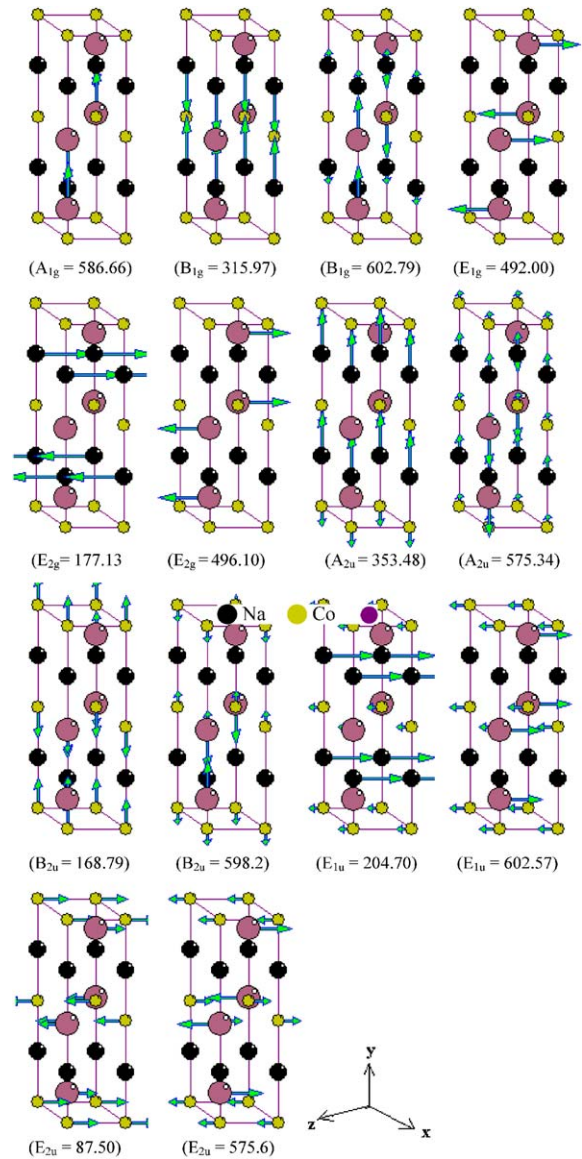


Fig. 1. Vibrational pattern of some selected zone center phonon modes.

present calculation is quite successful in reproducing the phonon modes at zone center except few discrepancies in comparison to the available experimentally measured values by using Raman scattering [23,24], infrared [20,25] and calculated values of Li et al. [28] by using first principles method. The vibrational pattern of zone center phonon modes are presented in Fig. 1.

3.2. Phonon dispersion curves

Fig. 2 presents the phonon dispersion curves of NaCoO_2 calculated by using the present approach described above. It can be revealed from Fig. 2 that the phonon modes are separated in two frequency groups similar to the first principles calculation [28]. The lower frequency group, which is up to about 370 cm^{-1} , is due to the acoustic phonons while the higher frequency group with frequencies between 490 and 650 cm^{-1} is due to optical phonons. These regions have been named as soft and hard phonons by the Li et al. [28]. As can be seen from the phonon dispersion curves that the phonon modes are more dispersive in $(qq0)$ and (qqq) directions of the Brillouin zone. It has been shown by Jorgensen et al. [33] and Huang et al. [34] from their structural studies that the Na atoms occupy two different sites 2d and 2b. To see the effect of different site occupancy by Na atoms, we also considered two geometries for the NaCoO_2 similar to the consideration of Li et al.

[28] in their first principles calculation. In first case (Geometry A) the sodium atoms occupy 2b site while in second case (geometry B) the sodium atoms occupy the 2d site [23] for which the PDCs are presented in Figs. 2 and 3, respectively, and discussed above. Figs. 2 and 3 reveal that there is no significant difference in the gross features of the phonon dispersion curves in these two geometries except that the behavior of some phonon modes particularly involves the Na atoms vibration. In addition, we notice that the some phonon modes give significantly different frequencies near the zone center for the two geometries, which is obviously due to the different atomic positions of the Na atoms.

3.3. Phonon density of states

In order to investigate the phonon properties, the understanding of phonon density of states is vital, as it requires the computation of phonon modes in the entire Brillouin zone. The calculated

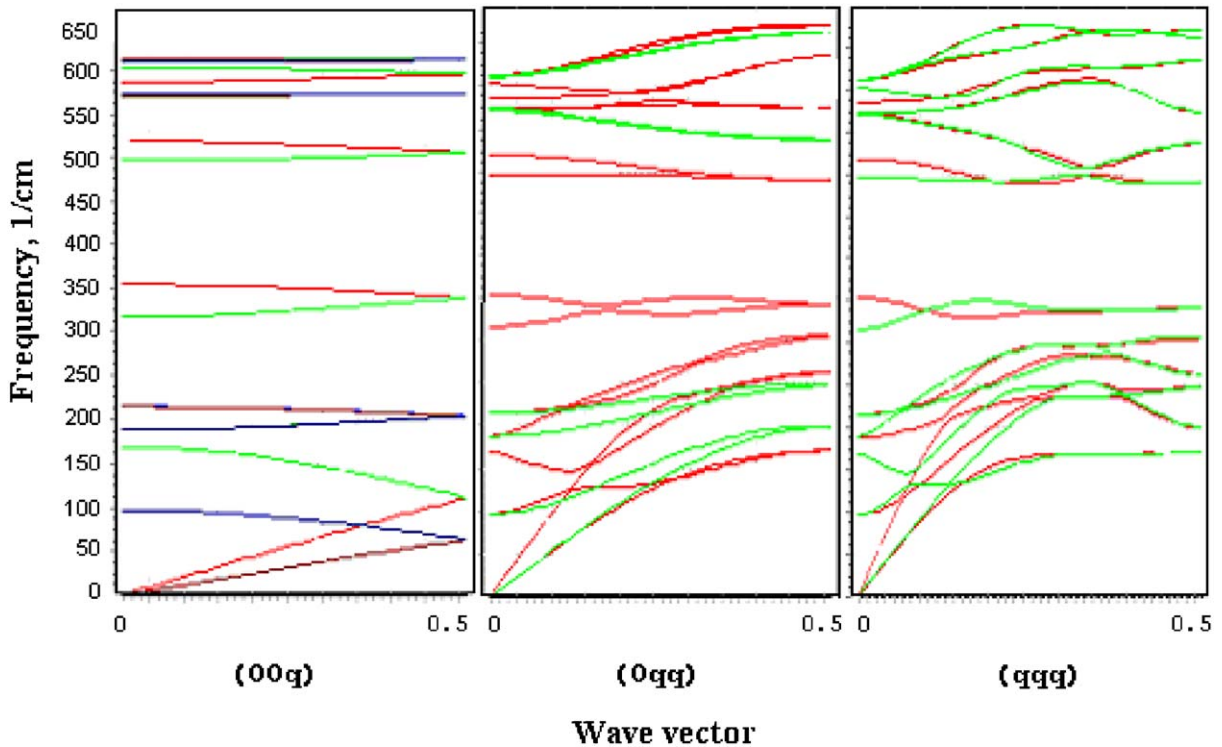


Fig. 2. Phonon dispersion curves of NaCoO_2 in considered geometry A.

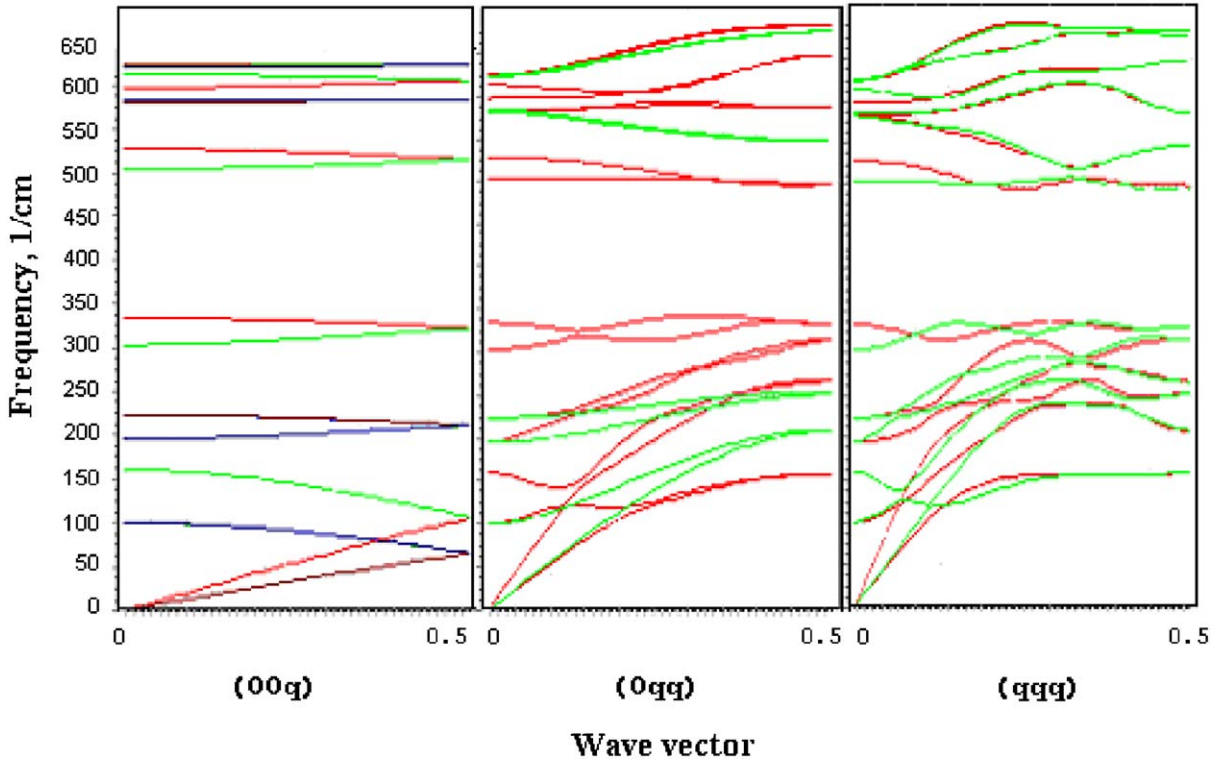


Fig. 3. Phonon dispersion curves of NaCoO₂ in considered geometry B.

total phonon density of states (DOS) and its partial components corresponding to the different atoms using the interatomic potential from Eq. (1) with parameters displayed in Table 1 are presented in Fig. 4. The latter are used to calculate the vibrational amplitudes of the different atoms as presented in Table 3 while the former are used to calculate the specific heat and Debye temperature. To understand the origin of peaks in the DOS, we examine the spectra of partial DOS displayed in Fig. 4 along with the total DOS. From a comparison of partial and total phonon DOS, it is clear that the total DOS has three different regions. The first region is below 200 cm^{-1} , where the peaks are mainly due to Co atoms with a small contribution from oxygen; the second region is between 200 and 370 cm^{-1} , where the contributions are mainly due to sodium atoms with some contribution from Co and O atoms, while the third and final region above 475 cm^{-1} is only due to Oxygen atoms. The contributions to frequency

ranges result from significant difference in atomic weight.

We have also calculated the neutron weighted phonon density of states (generalized phonon density of states) to compare with the experimentally measured GDOS to understand the success of the present predictions. The calculated GDOS for both geometries are presented in Fig. 5. The GDOS is bare DOS weighted with σ_i/M_i (scattering cross section over mass) and therefore the gross features in GDOS is similar to the total phonon DOS. It is seen from the Fig. 5 that there are two phonon groups similar to the experimental GDOS [24] and first principles DOS [28]. The present calculation similar to the first principles calculations [28] predicts low frequency DOS comparable to the experimental GDOS [24]. However, it seems that the present calculation is better in reproducing the higher frequency side of the spectra and compares well with the experimental DOS [24] in comparison to the first

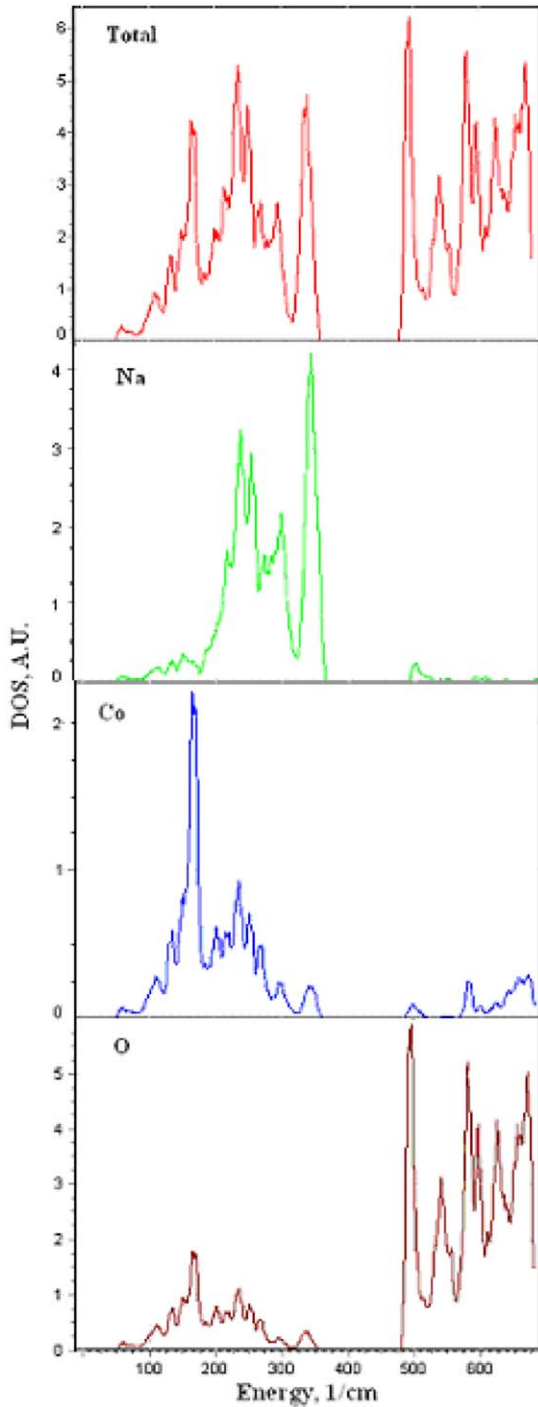


Fig. 4. Total and partial phonon density of NaCoO_2 compound.

Table 3
Vibrational amplitudes of the various atoms in NaCoO_2

Atoms	$8\pi^2\langle u^2 \rangle / 3$ (\AA^2)				
	2 K	50 K	100 K	200 K	300 K
Na	0.2191	0.2244	0.2446	0.3325	0.4464
Co	0.1056	0.1123	0.1360	0.2111	0.2965
O	0.1812	0.1869	0.2037	0.2575	0.3251

principal calculation [28] as far as range of DOS is concerned. The present calculation could also not predict the DOS up to 800 cm^{-1} as observed in the experimental spectra obtained from inelastic neutron scattering. As far as failure of these calculations in predicting the complete neutron scattering data [24] which show that the DOS goes zero at 100 meV is concerned, we believe that the scattering for greater than equal to 100 meV in INS measurement is due to the multiphonon scattering. We also notice significant changes in the lower frequency side of the phonon density of states in two different geometries. It can be seen from Figs. 5(a) and (b) that many of the peaks in lower frequency side of the spectra which are prominent in geometry A (Fig. 5(a)) either disappear or become weak in the case of geometry B (Fig. 5(b)). In addition, many peaks convert into the shoulders around the main peaks. However, we do not observe any significant change in the higher frequency side of the spectra.

3.4. Specific heat and Debye temperature

The temperature dependent lattice specific heat at constant volume of NaCoO_2 has been calculated by using the phonon density of states and can be expressed as

$$Cv(T) = K_B \int \left(\frac{h\omega}{2\pi K_B T} \right)^2 \times \left[\frac{\exp(h\omega/2\pi K_B T)}{(\exp(h\omega/2\pi K_B T) - 1)^2} \right] g(\omega) d\omega, \quad (3)$$

where $g(\omega)$ is the total phonon DOS. In Fig. 6, the heat capacity at constant volume with temperature

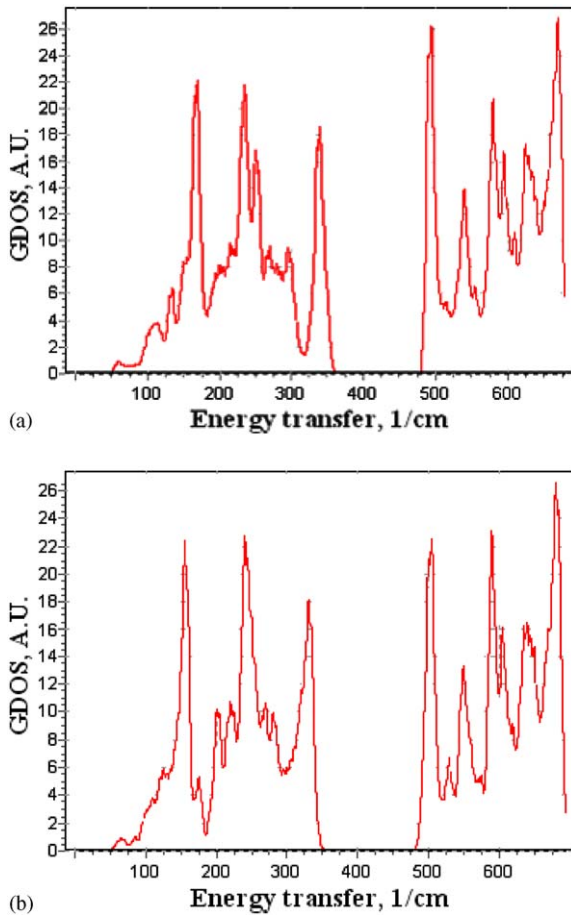


Fig. 5. Generalized Phonon density of States of NaCoO₂ (a) geometry A and (b) geometry B.

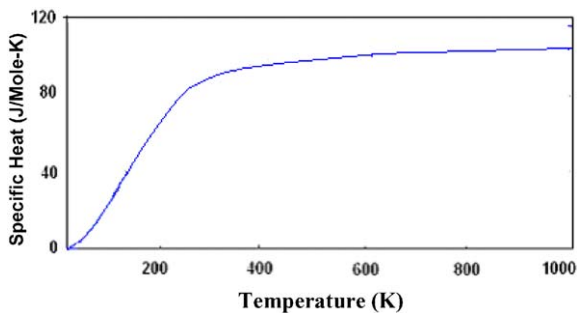


Fig. 6. The lattice Specific heat at constant volume of NaCoO₂.

is presented. To the best of our knowledge this is the first reported specific heat data for this compound. The Debye temperature at room

temperature has been calculated for NaCoO₂ from the present specific heat data. Our estimated value of Debye temperature θ_D is 793 K, which could not be compared with any experimental or theoretical data due to nonavailability. However, the Debye temperature of 793 K at room temperature suggests that the transport properties in insulating phase of cobalt oxide superconductor are dominated by electron–phonon interaction.

The computed partial phonon density of states is used to calculate the vibrational amplitudes of different species of NaCoO₂ compound and is presented in Table 3. This table reveals that the vibrational amplitudes increase with the increase in temperature similar to the experimental data [24]. The vibrational amplitudes do not behave anomalously in the studied temperature range.

4. Conclusions

In conclusion, we have investigated the phonon properties of the NaCoO₂ compound by using simple lattice dynamical model and obtained an overall consistent description of the phonon properties of this compound. The calculated zone center phonon frequencies are generally in good agreement with the available experimental data such as Raman and infrared and theoretical data. The generalized phonon density of states compare well with the experimental spectra and first principles calculated DOS. There is significant difference in the low frequency spectra due to Na site occupancy. In addition to phonon frequencies and DOS, we also report the lattice specific heat and Debye temperature for NaCoO₂ compound. The vibrational amplitudes of the different atoms of NaCoO₂ compound have also been reported and no anomalies have been observed in the studied temperature range.

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