

Density functional calculation of electronic structure and phonon spectra of Na₂OMeagan Thompson,^{1,*} Xiao Shen,² and Philip B. Allen²¹Department of Geosciences, Stony Brook University, Stony Brook, New York 11794-2100, USA²Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA

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We present a theoretical study of Na₂O (sodium oxide) using density functional theory with a plane-wave basis set; both the local-density approximation and the generalized gradient approximation were used for exchange and correlation. Cohesive energy, lattice parameter, electronic band structure, phonon spectra, phonon density of states, elastic constants, bulk modulus, Debye temperature, and specific heat are calculated. Results are in reasonable agreement with other calculations and experimental data, where data exist.

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I. INTRODUCTION

Sodium oxide, like the other alkali-metal oxides, crystallizes in the cubic antiperovskite structure. This structure exhibits fast ionic conduction, with potential applications such as solid-state batteries, gas detectors, and fuel cells. Despite its possible usefulness, Na₂O remains largely untouched experimentally, perhaps due to difficulties in preparation and preservation of Na₂O crystals. Cohesive energy is reported in the Handbook of Chemistry and Physics¹ and early powder-diffraction experiments by Zintl *et al.*² determined room-temperature lattice parameter. Barrie and Street³ reported core and electron binding energies as well as photoionization cross sections relative to the Na 1s energy level using Auger and photoelectron spectroscopies. However, little more was done with sodium oxide until computational abilities made quantum-mechanical calculations feasible. In 1991, Dovesi *et al.*⁴ computed binding energy, lattice parameter, bulk modulus, and phonon frequencies at $Q=0$ of the alkali-metal oxides using CRYSTAL, a Hartree-Fock (HF) linear combination of atomic orbitals (HF-LCAOs) computational package, which uses all-electron potentials. Bulk modulus and lattice parameter are in reasonable agreement with experiment where data exist. Shukla *et al.*⁵ explored electronic structure at the HF level using a Wannier-function (WF) basis to determine cohesive energies, lattice parameters, and bulk modulus of Li₂O and Na₂O. Results agreed well with Dovesi *et al.* In 2003, Mikajlo *et al.*⁶ filled in some of the gaps in experimental data by using electron momentum spectroscopy to determine electronic band structure. Results were compared with *ab initio* calculations performed using an updated version of CRYSTAL at the HF, density functional theory (DFT), and hybrid DFT levels. Most recently, Eithiraj *et al.*⁷ used the linear muffin-tin orbital in its tight-binding representation (TB-LMTO) to determine lattice parameter, bulk modulus, and electronic band structure of Li₂O, Na₂O, and Rb₂O.

II. CALCULATION

The present work determines lattice parameter, cohesive energy, electronic band structure, phonon spectra, phonon density of states (P-DOS), elastic constants, bulk modulus, Debye temperature, and specific heat using the plane-wave

self-consistent field (PW_{scf}) code. PW_{scf} is part of the QUANTUM ESPRESSO distribution,⁸ a suite of open source codes which solves self-consistent Kohn-Sham equations for a periodic solid within the DFT framework. A plane-wave basis set is used to expand the orbitals. We use Vanderbilt ultrasoft pseudopotentials⁹ and both local-density approximation (LDA) and the generalized gradient approximation (GGA) for exchange and correlation. For LDA, the Perdew-Zunger (PZ) (Ref. 10) scheme was used, while the GGA scheme is Perdew-Burke-Ernzerhof (PBE).¹¹ For sodium, the reference occupancy was chosen as $2s^2 2p^6 3s^1$, while the oxygen basis orbitals are $2s^2 2p^4$. For both LDA and GGA calculations, energy cutoffs are 30 Ry for wave functions and 420 Ry for charge density and a $10 \times 10 \times 10$ Monkhorst-Pack k -point grid is used. The error associated with both energy cutoffs and k -point sampling is 0.002 Ry.

III. RESULTS

Figure 1 shows electronic band spectra of Na₂O for the LDA calculations and Table I gives selected key energies. The occupied bands show relatively little dispersion, as expected in an ionic insulator. The band gap is direct at the Γ point and is between the cation “ p ”-like valence band and the anion “ s ”-like conduction band. The gap is smaller than ex-

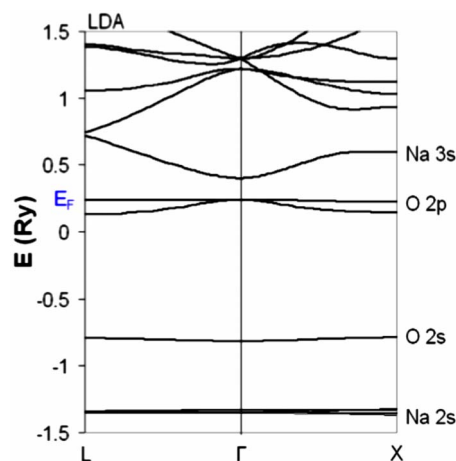


FIG. 1. (Color online) Electronic band structure from LDA calculation.

TABLE I. Comparison of cohesive energy E_{coh} , $k=0$ energy differences, bandwidths W and $Q=0$ IR and Raman phonon frequencies ν , and bulk modulus K between our results and previous calculations and experiments. K is calculated from the second derivative of total energy versus volume.

	Expt.	This Study		Mikajlo ^a			Eithiraj ^b	Dovesi ^c	Shukla ^d
		LDA	GGA	LDA	GGA	PBE0	TB-LMTO	LCAO	HF
E_{coh} (Ry)	0.6442 ^e	0.7383	0.6356					0.6642	0.3766
a (Å)	5.49 ^f	5.398	5.583	5.393	5.559	5.498	5.465	5.484	5.481
O $2p$ -O $2s$ (Ry)	1.165 ^a	1.055	1.073	1.046	1.068	1.777			
O $2s$ -Na $2p$ (Ry)	0.863 ^a	0.515	0.530	0.542	0.537	0.568			
Na $2p$ -Na $2s$ (Ry)	2.315 ^a	2.007	2.051	2.015	2.059	2.188			
E_g (Ry)		0.161	0.143				0.178		
$W(\text{O } 2p)$ (Ry)	0.044 ^a	0.044	0.045	0.074	0.071	0.079	0.036		
$W(\text{O } 2s)$ (Ry)		0.027	0.019	0.024	0.023	0.025			
$\nu(\text{Raman})$ (THz)		7.56	7.06					7.85	
$\nu(\text{IR})$ (THz)		9.18	8.17					9.56	
K (GPa)		56	54				59	58	61.1

^aReference 6.

^bReference 7.

^cReference 4.

^dReference 5.

^eReference 1.

^fReference 2.

pected for an insulator but is consistent with the gap calculated by Eithiraj *et al.*⁷ To our knowledge, no experimental band gap data exist for comparison. However, DFT routinely underestimates the band gap for insulators.¹² Table I compares cohesive energy, lattice parameter, and band gaps from this study with results from those listed above. Cohesive energies were determined by subtracting atomic energies from the equilibrium total energy per unit cell. Atomic energies were calculated with spin-polarized atoms, with oxygen being atomic. Results agree well with experiment and other calculations. The lattice parameter was optimized by relaxing the cell. The results compare well with room-temperature powder-diffraction experiments performed by Zintl *et al.*² which were later extrapolated to a zero-temperature lattice parameter of 5.49 Å by Dovesi *et al.*⁴ As expected, LDA underestimates the lattice parameter while it is overestimated by GGA. Band-structure results from this study agree well with the Mikajlo experiments and calculations⁶ as do Γ -point

energies. Energy differences between the O $2p$ and $2s$ like states are underestimated compared to experiment, as are those between Na $2s$ - $2p$ and O $2s$ -Na $2p$. Meanwhile, O $2p$ bandwidth agrees with experiment; O $2s$ bandwidth is consistent with calculations,⁶ but no experimental data exist for comparison.

Phonon spectra along symmetry lines from LDA calculations are shown in Fig. 2. Central-zone frequencies were calculated by Dovesi *et al.* in 1991 for the two lowest transverse optical modes only.⁴ While Γ -point phonon frequencies are comparable in magnitude, LDA agrees more closely with previous calculations. By fitting the dispersion curves of acoustic phonon modes close to Γ with linear functions, we obtain the acoustic velocities. Elastic constants were then calculated from the acoustic velocities using equations from Landau and Lifshitz.¹³ The results are shown in Table II. While there is no evidence in the literature that elastic constants have been determined for Na₂O, bulk modulus calcu-

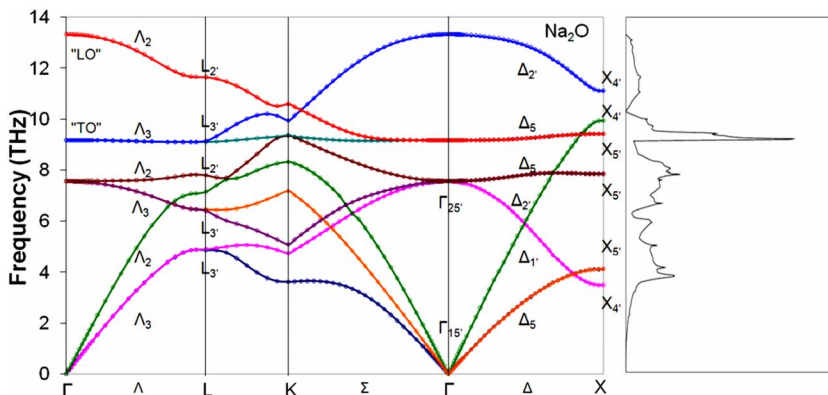


FIG. 2. (Color online) Phonon spectra along lines of high symmetry and phonon density of states from LDA calculation. The color shown on line follows the continuous crossing of the modes of different symmetries.

TABLE II. Elastic constants C_{11} , C_{12} , and C_{44} and bulk modulus K in GPa. $K = \frac{1}{3}(C_{11} + 2C_{12})$. Numbers in parentheses are errors associated with fitting.

	C_{11}	C_{12}	C_{44}	K
LDA	114(8)	37.8(1.3)	32.8(0.6)	63(4)
GGA	114(7)	34.7(1.3)	27.4(0.5)	61(3)

lated from elastic constants agree well with other calculations^{4,5,7} (see Tables I and II).

Using the elastic constants and phonon spectrum from our DFT calculations, we calculate the thermodynamic parameters of Na₂O under harmonic approximation. The specific heat of an insulator can be computed in harmonic approximation from the phonon density of states,

$$C(T) = \frac{k_B}{V_{\text{cell}}} \int_0^\infty d\Omega \mathcal{D}(\Omega) \left(\frac{\hbar\Omega/2k_B T}{\sinh(\hbar\Omega/2k_B T)} \right)^2, \quad (1)$$

where V_{cell} is the cell volume. The density of states is normalized as $3n = \int d\Omega \mathcal{D}(\Omega)$, where n , the number of atoms per cell, is 3 for Na₂O. At low temperature, the density of states scales as Ω^2 , with a coefficient that depends on the elastic constants. The corresponding specific heat is $C = (12\pi^4 n k_B / 5 V_{\text{cell}}) (T / \Theta_D)^3$. The Debye temperature Θ_D is related to elastic constants by a complicated angular average. An approximate version of this angular average is known to work well in cubic insulators.¹⁴ Additionally, Na₂O is quasi-isotropic, especially in the LDA; therefore, the use of the simplified formula is appropriate. Using Eq. (3) in Ref. 14, we find $\Theta_D = 559$ and 545 K for LDA and GGA, respectively.

At high T , the factor $\hbar\Omega/2k_B T$ is small over the whole spectrum, and the specific heat is $3nk_B/V_{\text{cell}}$, the DuLong-Petit value.

It is useful to define the moments $\langle \omega^n \rangle$ of the spectrum, and corresponding characteristic temperatures T_n , by

$$\langle \omega^n \rangle = (k_B T_n / \hbar)^n = \int d\Omega \mathcal{D}(\Omega) \Omega^n / \int d\Omega \mathcal{D}(\Omega). \quad (2)$$

Then the harmonic specific heat can be Taylor expanded at high temperatures, giving the first correction

$$C(T) = \frac{3nk_B}{V_{\text{cell}}} \left[1 - \frac{1}{12} \left(\frac{T_2}{T} \right)^2 + \dots \right]. \quad (3)$$

From our predicted spectrum for Na₂O (LDA), we find $T_2 = 377$ K.

Another important quantity is the absolute harmonic entropy, which at high T can be written as $S = 3Nk_B \log(T/T_{\text{log}})$. The logarithmic temperature is $k_B T_{\text{log}} = \hbar \omega_{\text{log}}$, where the logarithmic average is the limit as n goes to zero of $\langle \omega^n \rangle^{(1/n)}$, or

$$\omega_{\text{log}} = \exp(\log \omega). \quad (4)$$

For LDA, we find $T_{\text{log}} = 332$ K.

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