

Ab-initio Electronic Structure Calculations of α -, β - and γ - KNO_3 Energetic Materials

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Abstract: We have computed energy bands and density of states (DOS) of different temperature dependent phases (namely α , β and γ) of potassium nitrate (KNO_3). The band structure computations have been performed using linear combination of atomic orbitals scheme within density functional theory (LCAO-DFT) with local density approximation and generalized gradient approximation. Moreover, to see the role of hybrid Hartree Fock and DFT Hamiltonian, we have employed Becke's three parameter hybrid functional calculations. The present LCAO-DFT calculations indicate that there exists a direct band gap for α - and γ - KNO_3 , while in the case of β - KNO_3 an indirect band gap is found. It is observed that the LCAO-GGA calculations show a better agreement with the experimentally observed band gap. An explosive nature of KNO_3 is also discussed in terms of energy bands and density of states.

Keywords: Band structure calculation, Linear combination of atomic orbitals, Density functional theory, Potassium nitrate.

1. Introduction

Potassium nitrate (KNO_3) is a well known ingredient in explosives and propellants, including black powder and other early forms of gunpowder. It is also used to enhance fertility of soil and an oxidizing agent in pyrotechnics. The metastable phase has been extensively studied due to its ferroelectric properties, however it has been difficult to take any advantage due to lack of stability.

KNO_3 can exist in three different phases namely, α , β and γ , depending on the temperature. At room temperature, KNO_3 crystallizes into α -phase (also called phase II).¹ The unit cell of α phase has an aragonite Pmcn (62) orthorhombic structure. On heating up to 128 °C, it transforms from α -phase to a trigonal structure so called β - KNO_3 (also known as

phase I) which exists up to 200 °C. Between these two phases a trigonal phase (γ -KNO₃ or phase III with a space group R3m (160)² also exists between 100 and 124 °C, which shows ferroelectric properties. A neutron diffraction study by Adiwidjaja and Phol demonstrated that the crystal structure actually consists of a 2x2x1 super cell of the Pmcn unit cell with Z=16 and with a the space group Cmc2₁.³

Among earlier studies, Balkanski et al.⁴ has studied phase transition in various phases of KNO₃ using Raman scattering method. Raman study of α -KNO₃ has been reported by Brooker⁵, using theory of local electron density functional, the band structure and density of states (DOS) of alkali nitrate have been calculated by Zhuravlev and Poplavnoi⁶. Pak and Nevostuev⁷ have studied formation and decay of radicals in KNO₃. Lu and Hardy⁸ developed an ab-initio theoretical description for both the α - and γ -KNO₃ and their transition to the higher temperature disordered phase I through static structural relaxations and molecular dynamical simulations. Liu et al.⁹ measured the Raman spectrum of KNO₃ at room and liquid nitrogen temperatures and performed the lattice dynamical calculation based on the rigid ion approximation and empirical potentials. A theoretical study of structural and dielectric properties of phase III of KNO₃ has been reported by Dieguez and Vederbilt.¹⁰ Aydinol et al.¹¹ has investigated the electronic structure and stability of various phases of KNO₃ using SIESTA package which is a pseudopotential self consistent DFT code with local orbitals. The electronic band structure and optical properties of the ferroelectric phase III of KNO₃ have been calculated by the first principal pseudopotential method using density functional theory (DFT) under generalized gradient approximation (GGA) and local density approximation (LDA) by Erdinc and Akkus.¹² Electronic structure of α -KNO₃ has been investigated employing PBE-GGA density functional by Lovvik et al.¹³

The data reported so far by different workers differ significantly which has led to several confusions related to electronic structure of KNO₃. To shed more light on the electronic structure, in the present paper, we report detailed band structure calculations of KNO₃ using the LCAO with DFT and hybridization of Hartree Fock (HF) and DFT.

2. Theoretical Methodology

2.1. LCAO using CRYSTAL03 Package

The CRYSTAL03 package¹⁴ is based on the LCAO approach which includes different types of schemes such as HF and DFT with LDA, and GGA, and also *posteriori* Becke's three parameter hybrid functionals

(B3LYP). In the present LCAO calculations, the crystal wave functions (ψ_k) are derived by solving the one electron time-independent Schrödinger equation,

$$(2.1) \quad \hat{h}\psi_k(\vec{r}) = \epsilon\psi_k(\vec{r}),$$

Here, the ψ_k follows the Bloch theorem having the form

$$(2.2) \quad \psi_k(\vec{r} + \vec{a}) = \psi_k(\vec{r}) \left[\exp(i\vec{k} \cdot \vec{a}) \right],$$

where $\vec{k}$ and $\vec{a}$ represent the wave vector and the translation vector, respectively. The HF, DFT (with LDA and GGA), and hybridization of HF and DFT (B3LYP) differ with each other in the definition of the Hamiltonian operator $\hat{H}$.

In the HF method, the exact interaction between the electrons is considered while correlation effects are neglected. In the HF scheme, $\hat{H}$ is defined as

$$(2.3) \quad \hat{H}_{\text{HF}} = \hat{T}_e + \hat{V}_{\text{ext}} + \hat{J}\{\rho(\vec{r})\} + \hat{K}_{\text{HF}}\{\rho(\vec{r}, \vec{r}')\},$$

where $\hat{T}_e$, $\hat{V}_{\text{ext}}$, $\hat{J}$ and $\hat{K}_{\text{HF}}$ represent the operators for kinetic energy of the electron, external potential due to electron-nuclei interaction, coulomb and non-local exchange energies, respectively. In the Kohn-Sham approach of DFT, a variation is achieved in the $\hat{H}$ by replacing the operator $\hat{K}_{\text{HF}}$ in the above equation by $\hat{V}_{\text{xc}}$. The modified $\hat{H}$ is defined as

$$(2.4) \quad \hat{H}_{\text{KS-DFT}} = \hat{T}_e + \hat{V}_{\text{ext}} + \hat{J}\{\rho(\vec{r})\} + \hat{V}_{\text{xc}}(\vec{r}),$$

Here $\hat{V}_{\text{xc}}$ is the exchange-correlation potential operator and is obtained by partially differentiating the exchange-correlation density functional energy $E_{\text{xc}}(\rho)$ with respect to the electronic density at any point $\vec{r}$. Mathematically,

$$(2.5) \quad \hat{V}_{\text{xc}}(\vec{r}) = \frac{\partial E_{\text{xc}}(\rho)}{\partial \rho(\vec{r})},$$

This $E_{\text{xc}}(\rho)$ includes various energies such as energy due to electron exchange, electron correlation, self-interaction, etc. Within the LDA and GGA schemes, the $E_{\text{xc}}(\rho)$ is given

$$(2.6) \quad E_{XC}^{LDA}(\rho) = \int_{\text{unitcell}} \rho(\vec{r}) E_{XC}\{\rho(\vec{r})\} d\vec{r},$$

$$(2.7) \quad E_{XC}^{GGA}(\rho) = \int_{\text{unitcell}} \rho(\vec{r}) E_{XC}\{\rho(\vec{r}), |\nabla\rho(\vec{r})|\} d\vec{r},$$

E_{XC} represents the exchange-correlation energy per particle. In the present DFT-LDA calculations, we have employed Dirac-Slater exchange¹⁴ and Perdew-Zunger¹⁵ correlation potentials. In the DFT-GGA scheme, we have chosen the exchange potential given by Becke¹⁶ and the correlation potential by Perdew-Wang.¹⁷ To judge the effect of hybridization of HF and DFT, we have chosen the B3LYP approach where, $E_{XC}(\rho)$ is defined as

$$(2.8) \quad E_{XC}^{B3LYP}(\rho) = 0.80 \left[E_{XC}^{BECKE} + 0.90 \Delta E_{XC}^{BECKE} \right] \\ + 0.20 E_{XC}^{HF} + 0.19 E_{XC}^{VWN} + 0.81 E_{XC}^{LYP},$$

E_{XC}^{HF} , E_{XC}^{LDA} and E_{XC}^{BECKE} are the exchange energies for the HF, Dirac-Slater and Becke, respectively while E_{XC}^{VWN} and E_{XC}^{LYP} represents the correlation energies of Lee-Yang-Parr¹⁸ and Vosko-Wilk-Nusair.¹⁹ The prefactors correspond to standard hybridization of HF/DFT. The lattice parameters for the α -KNO₃ were taken to be $a = 5.414$, $b = 9.166$ and $c = 6.431$ Å, while the respective parameters for trigonal β - and γ -KNO₃ are $a = b = 5.425$, $c = 9.836$ Å and $a = b = 5.487$, $c = 9.156$ Å. We have used the all electron Gaussian basis sets for K, N and O taken from www.tcm.phy.cam.ac.uk / ~ mdt 26/basis sets. All the basis sets were optimized to achieve the lowest energy for stability of the system. The self-consistent calculations have been performed at 125 $\vec{k}$ points for α -KNO₃ and 65 $\vec{k}$ points for β - and γ -KNO₃ in the irreducible Brillouin zone.

3. Results and Discussion

3.1. Electronic band structure

In figures 1-3, we have shown the energy bands and density of state (DOS) of α , β and γ phases of KNO₃ calculated using the LCAO-GGA scheme. The LCAO based energy bands and DOS have been plotted using DL-visualize software. It is seen from DOS that the top of valence bands

and bottom of conduction bands are mainly determined by p orbitals. From these bands and DOS it is observed that:

- (a) The group of uppermost valence bands of α , β and γ phases of KNO_3 (just below the E_F) contains O (2p) states predominantly with a small contribution from K (4p, 3d) states.
- (b) The next valence band region (-1.5 to -2.5 eV) for α - and γ - KNO_3 is mainly composed of O (2p) states with a small contribution from N (2p) and K (4s, 4p, 3d) states.
- (c) In all the structures, the lower valence bands around -8 eV arise from hybridization of O (2s, 2p) and N (2p) states, characterizing the sp overlap.
- (d) The group of conduction bands (just above E_F) is formed from hybridization of O (2p) and N (2p) states for α - KNO_3 , and O (2p) and N (2s, 2p) states for γ - KNO_3 . The higher conduction bands for α and γ - KNO_3 and the total conduction bands in case of β - KNO_3 consist of strong hybridization of O (2p), N (2p, 2s) and K (4s, 4p, 3d) states.

The present bands and DOS confirm strong N-O and K-O interactions at low energies which lead to an explosive nature of KNO_3 . The LCAO-DFT-GGA calculation show a direct band gap at Γ (0, 0, 0) point for α - KNO_3 ; and at Z (1/2, 1/2, 1/2) point for γ - KNO_3 . On the contrary, β - KNO_3 shows an indirect band gap between Γ (0, 0, 0) and D (1/2, 1/2, 0) points.

In table 1, we have collated our computed band gap data along with experimental and theoretical data. As expected, the HF approach largely overestimates the band gap. It is seen that the B3LYP theory overestimates the band gaps in comparison to LCAO-GGA/LDA theories. The overestimation in B3LYP scheme can be understood in terms of mixing of HF with DFT Hamiltonian. It is seen that the LCAO-GGA calculations show a good agreement with the experimentally observed band gap.

Various abbreviations used in the table are:

LCAO-	Linear combination of atomic orbitals.
VASP-	Vienna ab initio software package.
PAW-	Projector augmented wave.
PP-	Pseudopotential.
DFT-	Density functional theory.
GGA-	Generalized gradient approximation.

LDA- Local density approximation.

Table 1. Energy band gap ΔE_g (in eV) for various phases of KNO_3

Scheme	Hamiltonian	$\alpha - \text{KNO}_3$	$\beta - \text{KNO}_3$	$\gamma - \text{KNO}_3$
Present LCAO	DFT-GGA	3.24	1.25	1.89
	DFT- LDA	3.07	1.03	1.77
	B3LYP	5.40	2.64	3.97
	HF	14.98	9.20	13.49
Available theory				
(a) PP-DFT (SIESTA) ¹¹	LDA	1.68	2.03	2.10
(b) Self consistent norm conserving PP ¹²	PBE-GGA	-	-	1.76
(c) PAW(VASP) ¹³	PBE-GGA	3.0	-	-
Experiment radical kinetics ⁷		≈ 4		

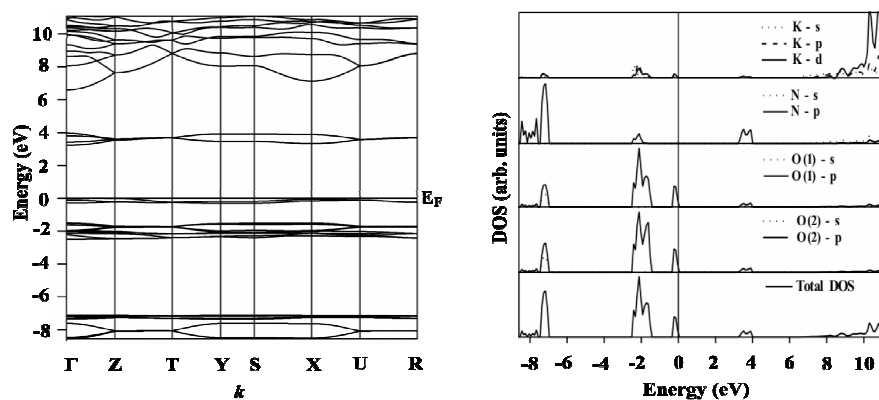


Fig. 1 Energy bands and DOS of $\alpha\text{-KNO}_3$ along high symmetry directions of the first Brillouin zone calculated using LCAO-GGA method. Here Γ (0,0,0), Z (0,0,1/2), T (-1/2,0,1/2), Y (-1/2,0,0), S (-1/2,1/2,0), X (0,1/2,0), U (0,1/2,1/2), R (-1/2,1/2,1/2), are featured k points in the Brillouin zone

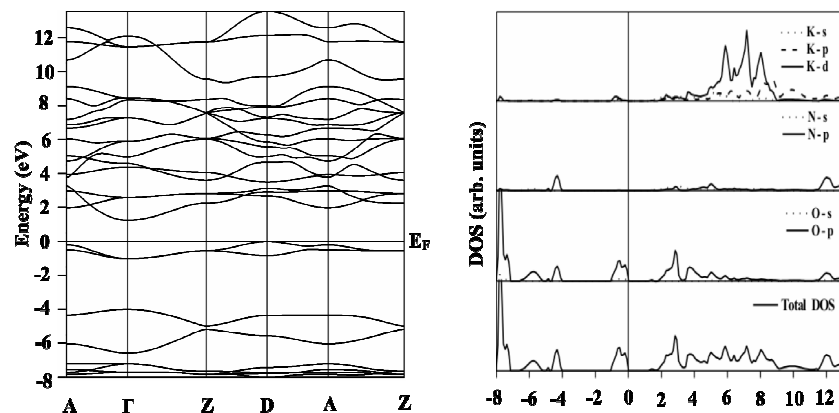


Fig. 2 Energy bands and DOS of β -KNO₃ along high symmetry directions of the first Brillouin zone calculated using LCAO-GGA method. Here A (1/2,0,0), Γ (0,0,0), Z (1/2,1/2,1/2), D (1/2,1/2,0) are featured k points in the Brillouin zone.

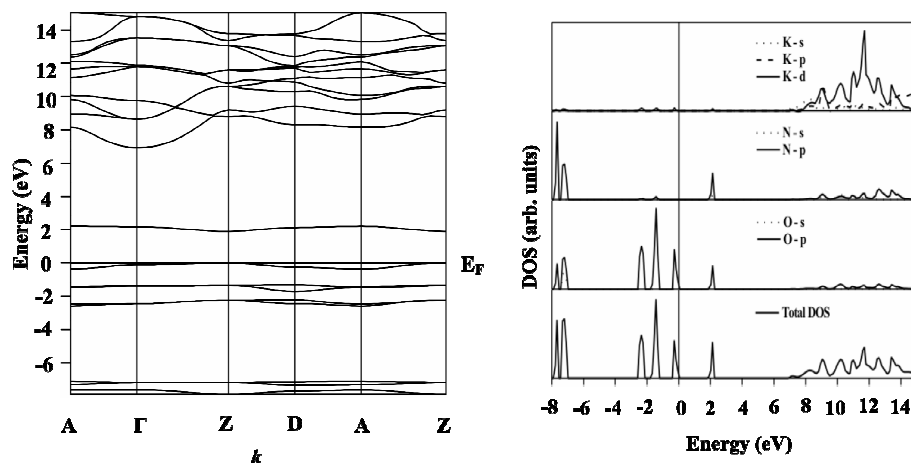


Fig. 3 Energy bands and DOS of γ -KNO₃ along high symmetry directions of the first Brillouin zone calculated using LCAO-GGA method. Here A (1/2,0,0), Γ (0,0,0), Z (1/2,1/2,1/2), D (1/2,1/2,0) are featured k points in the Brillouin zone.

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