Theoretical Investigation Of The Insulator-Metal Transition Point Of Nickel Monoxide

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Abstract

The study of the effects of applying high pressure by compression on materials is fundamental to a range of problems in condensed matter physics, materials science, technology, etc. Transition of an insulator into a metallic state is in general a basic phenomenon related to a wide range of physical systems. Nickel monoxide has been studied at different volume compression ratios by employing optical spectra and electronic structure calculations using the density functional theory implemented in the MindLab 5 code that made use of the local density approximation plus the Hubbard on-site Coulomb interaction parameter. Insulator-metal transition point was recorded at 0.60 volume compression ratio from both calculations and a transition pressure of 271 GPa was obtained using the Murnaghan equation of state.

Keywords: nickel monoxide, volume compression ratio, insulator-metal transition, electronic structure, optical spectra.

Introduction:

The physical properties of some materials undergo a variety of changes when they are subjected to pressure due to compression. The increase in compression on these materials means a significant decrease in the volume, which result in changes in their electronic states and crystal structure (Huotari *et al*., 2014). The compression can be either hydrostatic in which case the material retains its initial shape only, but the volume reduces or axial in which case the volume reduces and the shape of the material also changes (Gogotsi and Domnich, 2012).

Nickel monoxide (NiO) which is a member of the first row transition metal oxides (TMOs) possesses a unique variety of physical properties. The partially filled 3*d* shells overlap with the oxygen 2*p* and the nickel 4*s* to evoke an intricate interplay between lattices, orbital and spin degrees of freedom (Rödl and Bechstedt, 2012). Despite its partially filled 3*d* shells,

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NiO is insulating above as well as below the Néel temperature (T_N). NiO has a T_N of about 250^0C, above which it has a cubic rocksalt structure. The magnetic transition is accompanied by structural distortions that are yet to be fully understood from a theoretical point of view (Schrön *et al*., 2012). NiO in its natural state acts as an insulator in which case it does not allow electrons to readily flow through its inner structure. As a metal, its interior changes drastically, enabling currents to pass through it efficiently.

Pressure induced insulator-metal transition (IMT) is one of the most interesting phenomenon exhibited by matter under extreme pressure conditions (Feng and Harrison, 2004). The electronic structure of the material can be changed from its original state by modifying its density by external pressure (Huotari *et al*., 2014). Thus applying pressure is a way to tune a material's property. If this transition pressure is known, NiO can be used industrially as a pressure switch that closes an electrical contact when the set transition pressure has been reached. The NiO pressure switch can be designed such that when the set transition pressure is detected, the switch works to open or close the circuit. This allows it to work as a safety device, alarm or as a control element within the system. NiO also finds application in high temperature superconductors, electro-chromic display devices and transparent conductive electrodes as well as in parts of functional sensor layers in chemical sensors (Jandow, 2015). Attractive features of NiO include excellent durability and electro-chemical stability, low material cost, promising ion storage capacity, large span optical density and the possibility of manufacturing by a variety of techniques (Patil and Kadam, 2002).

Though there were suggestions of the metallic high pressure phase of NiO by de Boer and Verwey (1937) and the prediction of possible IMT by Mott (1956), the volume compression ratio or pressure at which this material will undergo IMT was not known. Cohen *et al*. (1997) carried out local density approximation (LDA) and generalized gradient approximation (GGA) calculations on the magnetic collapse of NiO and predicted a pressure of 230 GPa for magnetic collapse to occur. However, conventional LDA and GGA calculations failed to predict the correct ground state of some strongly correlated systems (Feng and Harrison, 2004). The LDA failed to describe the band structure of NiO as an insulator and predicted it to be a metal (Terakura *et al*., 1984; Shen *et al*., 1991). This deficiency of the LDA is not fully solved by the GGA, which still provides small band gap for NiO, indicating a metal as well (Leung *et al*., 1991; Dufek *et al*., 1994; Bredow and Gerson, 2000). Furthermore, Feng and Harrison (2004) predicted that NiO will undergo IMT at a volume compression ratio of approximately 0.65 from calculation using the B3LYP (Becke, 3-parameter, Lee-Yang-Parr) hybrid density functional. They also obtained a volume compression ratio of approximately 0.40 using the PWGGA (Perdew-Wang generalized gradient

approximation) method. Their results are contradictory with two different predicted volume compression ratios for NiO to undergo IMT (Gavriliuk *et al.*, 2012), thus leaving the subject matter open for further studies. Thassana and Techitdheera (2012) attempted the problem by focusing only on the effect of volume compression on the spin and orbital magnetic moments of NiO using the local spin density approximation plus the Coulomb interaction (LSDA+U). They concluded that NiO would undergo collapse in spin and orbital magnetic moments at a volume compression ratio of 0.80. However, they did not consider the volume compression ratio for IMT to occur in NiO. Also, Gavriliuk *et al.* (2012) detected IMT experimentally for the very first time at a pressure of approximately 240 GPa. This was achieved by applying an enormous amount of pressure on thin NiO single crystal samples in a thin platelet shape with a thickness of about 1 μm or less using a custom diamond anvil cell. They however suggested that further experimental and theoretical studies be considered or employed to confirm the transition pressure they so obtained or otherwise.

In this paper therefore, we intend to determine theoretically the volume compression ratio and pressure at which NiO will undergo IMT using the MindLab 5 code within the LDA+U approach.

Methods and Computational Details:

All calculations of the electronic band structure and optical spectra for NiO based on the LDA+U within the DFT approach were performed using the MindLab 5 code developed by Savrasov (1996), which utilizes the full-potential linearized Muffin-tin orbital (FP-LMTO) program, LMTART (Delin *et al.*, 1998). The calculation assumed NiO as an anti-ferromagnetic material with a lattice constant of 0.417 nm in the absence of distortion and the Muffin-tin radii of nickel and oxygen ions were 0.115 nm and 0.094 nm respectively. The volume compression ratio was defined by v/v_0, where v is the compressed volume and v_0 is the initial volume of the material before it was subjected to pressure due to volume compression. In the FP-LMTO method, all electrons are treated; including tightly bound inner core electrons, loosely bound outer core electrons and itinerant valence electrons. This is to ensure that their rapidly changing character under compression is fully accommodated. Different volume compression ratios were used in performing the calculation to determine their effects on the electronic structure and optical spectra of NiO. The Coulomb potential binding the electron-electron pair decreases as the pressure is increased by volume compression. This could be attributed to the spacing in the electrons' positions r_i and r_j. As further pressure is applied, the electrons' spacing ($|r_i - r_j|$) becomes infinitely large, leading to a collapse of the Coulomb

potential binding the electrons thereby leading to an increase in the energy of the electrons upon compression. This is summarized by the Hamiltonian

$$H_{sys} = T + U(r) \qquad (1)$$

where

$$T = -\frac{\hbar}{2m_e} \sum_i \nabla_i^2 \qquad (2)$$

and

$$U(r) = \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} \qquad (3)$$

T is the kinetic energy of the electrons, $U(r)$ is the electron-electron interaction potential, m_e is the electron mass, r_i is the position of the ith electron and r_j is the position of the jth electron.

As the material is compressed further, there is sufficient increase in pressure which tends to further reduce the electron-electron potential and making the electrons to now possess maximum kinetic energy. This makes the electrons to be delocalized; then ionized in the process and thus leading to metallization.

To obtain the transition pressure, the volume compression ratio so obtained at the point of IMT is then fit into the Murnaghan equation of state (EOS) (Murnaghan, 1944) in equation (4) rather than the Birch-Murnaghan EOS (Birch, 1947) or the Vinet EOS (Vinet *et al.*, 1989) in equations (5) and (6) respectively.

$$P = \frac{B_0}{B_0'} \left[\left(\frac{v}{v_0} \right)^{-B_0'} - 1 \right] \qquad (4)$$

$$P = \frac{3}{2} B_0 \left[\left(\frac{v_0}{v} \right)^{7/3} - \left(\frac{v_0}{v} \right)^{5/3} \right] \left[\frac{3}{4} (B_0' - 4) \left\{ \left(\frac{v_0}{v} \right)^{2/3} - 1 \right\} + 1 \right] \qquad (5)$$

$$P = 3 B_0 \left(\frac{v_0}{v} \right)^{2/3} \left[1 - \left(\frac{v}{v_0} \right)^{1/3} \right] \exp \left[\frac{3}{2} \{ B_0' - 1 \} \left\{ 1 - \left(\frac{v}{v_0} \right)^{1/3} \right\} \right] \qquad (6)$$

Here B_0 is the isothermal bulk modulus, B_0' is the first derivative of B_0 at $P = 0$, v/v_0 is volume compression ratio. Though all three EOS above give favourably results at high pressure (Zhuravlev, 2007), a major limitation of the Birch-Murnaghan EOS and the Vinet EOS is their inability to take into account phase transition induced by pressure (Stacey, 1981). The reason being that Birch-Murnaghan EOS and Vinet EOS were modified from the Murnaghan EOS and one of the assumptions during the modification is that they are strictly derived for isotropic materials (Stacey, 1981).

The activation energy for conduction, ε, according to Mott (1980) is given by

$$\varepsilon = E_C - E_F \qquad (7)$$

and the band gap is given as

$$E_g = E_C - E_V \qquad (8)$$

E_c is the lowest value of energy in the conduction band, E_V is the highest energy value in the valence band and E_F is the Fermi energy level.

Results and Discussion:

The electronic band structure and optical spectra of NiO have been computed for different volume compression ratios in steps of 0.05 with the assumption that:

i.   the compression was hydrostatic; that is the material retains its cubic shape throughout the compression

ii.   the compression was done isothermally.

Figures 1 – 4 show the electronic structures of NiO at 0.50 – 0.65 volume compression ratios respectively. The broken line represents the Fermi energy level which is referred to as the minimum energy level required for an electron to be excited into the conduction band from the valence band. The conduction band of NiO is predominantly occupied by the Ni (*3d*) state while the valence band is predominantly occupied by the O (*2p*) state.

As pressure applied on NiO by volume compression was increasing, it was observed that the Fermi energy level continued to move towards the conduction band and away from the valence band. That is, the Ni (*3d*) density decreases towards the Fermi level and pushed down to higher binding energy. Simultaneously, the O (*2p*) density increases towards the Fermi level making NiO to be ionic or to possess a charge transfer character.
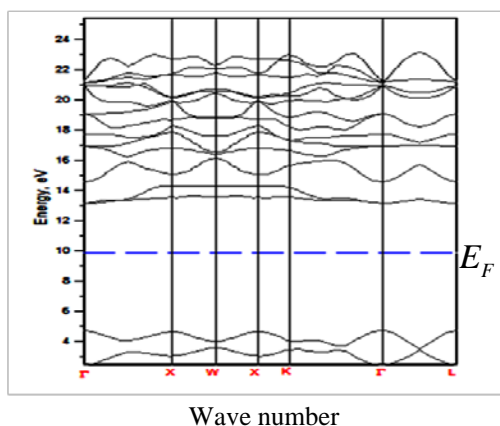

Fig. 1: Electronic band structure of NiO at 0.50 volume compression ratio.
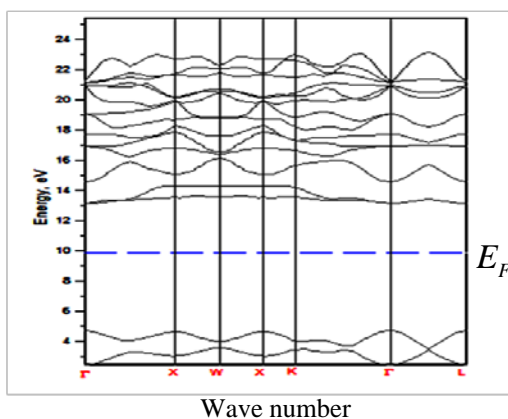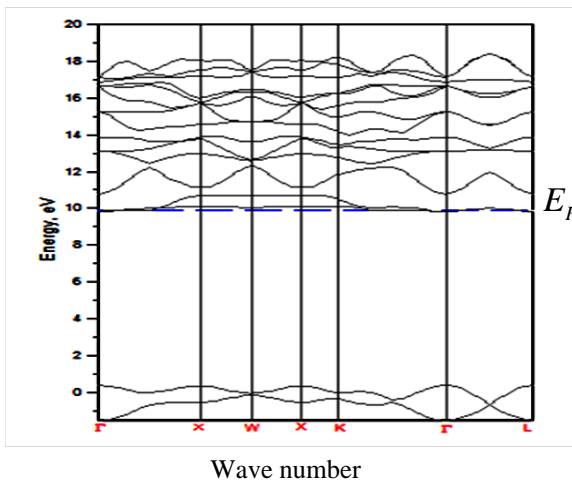

Fig. 2: Electronic band structure of NiO at 0.55 volume compression ratio.

At a volume compression ratio of 0.50 as presented in Figure 1, ε was calculated to have a value of 3.17eV. In Figure 2, it was observed that the Fermi energy level had moved further towards the conduction band as pressure due to volume compression was increased and ε was calculated to be 1.45eV. Moreso, at 0.60 volume compression ratio, it was observed that the Fermi energy level now intersects the conduction band. This is illustrated in Figure 3 with ε calculated to be zero. However, if the Fermi energy level intersects the conduction band, the system or material becomes conducting or becomes a metal (Meredith *et al.*, 2013). This assertion was also explained by Mott (1980), where he proposed that in the insulating range at high pressure, the conductivity of NiO behaves like

$$\sigma = \sigma_{min} \exp\left(-\frac{\varepsilon}{PV}\right) \tag{9}$$

where ε goes continuously to zero as transition is approached. Thus NiO becomes conducting at 0.60 volume compression ratio.

Wave number

Fig. 3: Electronic band structure of NiO at 0.60 volume compression ratio.
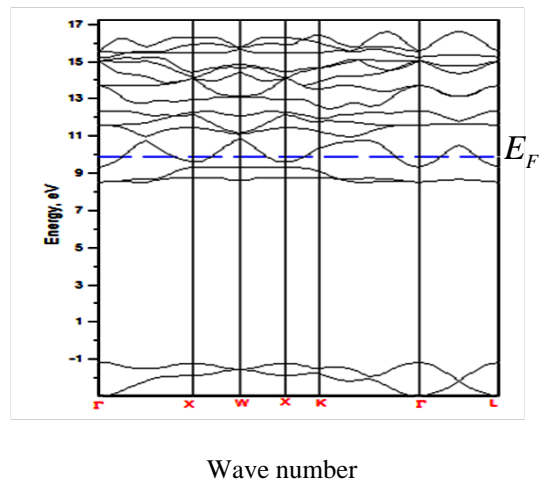
Fig. 4: Electronic band structure of NiO at 0.65 volume compression ratio.

We confirmed this volume compression ratio of 0.60 for IMT to occur by employing optical spectra calculation. Figures 5 – 10 show the electron energy loss spectra of NiO at 0.50 – 0.70 volume compression ratios respectively. The electron energy loss spectrum which is calculated from the imaginary part of the dielectric function describes the drift of electrons which is as a result of the different volume compressions. This can be observed from the waveform pattern displayed in the electron energy loss spectra.
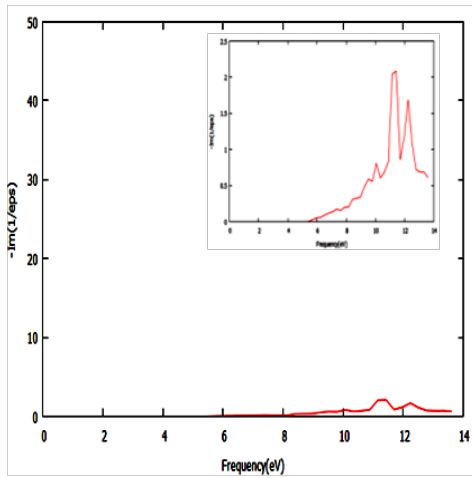
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Fig. 5: Electron energy loss spectrum of NiO at 0.50 volume compression ratio. Inset shows enlarged region up to a peak value of 2.50.
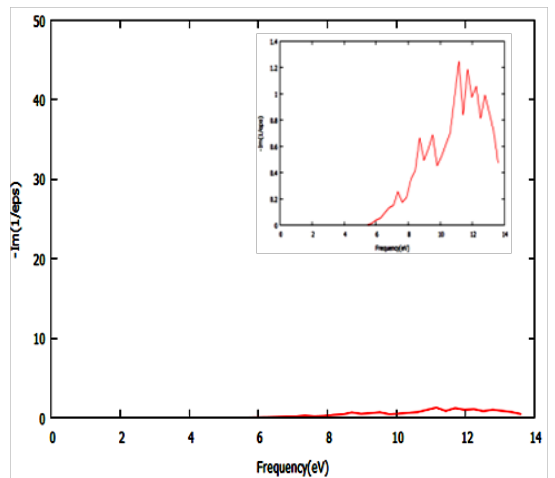

Fig. 6: Electron energy loss spectrum of NiO at 0.55 volume compression ratio. Inset shows enlarged region up to a peak value of 1.40.
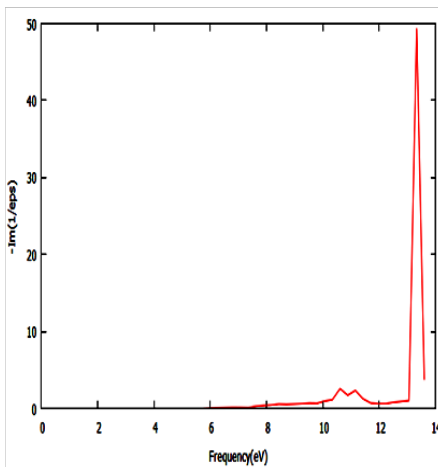

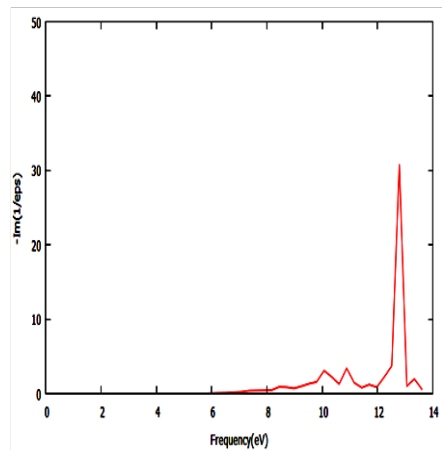Fig. 7: Electron energy loss spectrum of NiO at 0.60 volume compression ratio.

Fig. 8: Electron energy loss spectrum of NiO at 0.65 volume compression ratio.
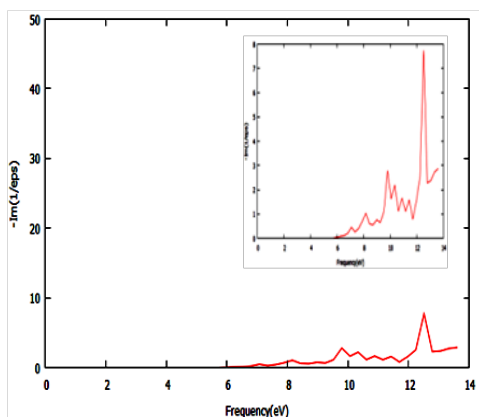
Fig. 9: Electron energy loss spectrum of NiO at 0.70 volume compression ratio. Inset shows enlarged region up to a peak value of 8.
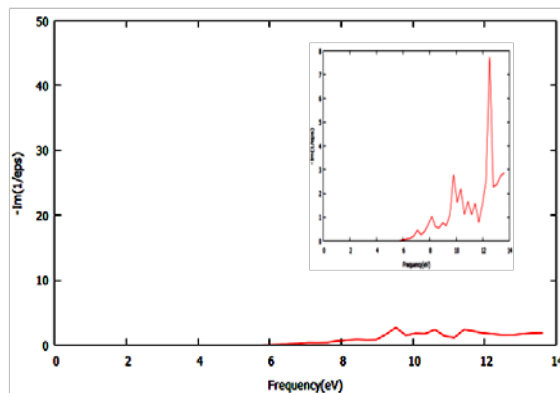
Fig. 10: Electron energy loss spectrum of NiO at 0.75 volume compression ratio. Inset shows enlarged region up to a peak value of 3.

Figures 5 and 6 show the electron energy loss spectra of NiO at 0.50 and 0.55 volume compression ratios respectively. It can be observed that at 0.50 volume compression ratio, the highest peak of the electron energy loss spectrum is about 2.50 units which thereafter dropped to 1.40 units at a volume compression ratio of 0.55. This describes the drift of electrons as pressure due to volume compression was applied on the material. At 0.60 volume compression ratio, a sharp rise was observed in the electron energy loss spectrum with a peak value of around 49.5 units as shown in Figure 7. This sharp rise is associated with inter-band transition which describes the energy loss of fast drifting electrons traversing the material from the valence band to the conduction band (Mooradian and Fan, 1966). Figure 8 shows a drop in peak to about 32.5 units in the electron energy loss spectrum with further increase in pressure due to volume compression. This was achieved at a volume compression ratio of 0.65. This drop in peak in the electron energy loss spectrum continues as pressure due to volume compression increases as shown in Figure 9 with electron energy loss spectrum peak value of about 8 units and Figure 10 with electron energy loss spectrum peak value of about 3 units at volume compression ratios of 0.70 and 0.75 respectively.

From our electronic structure calculation, we obtained IMT at a volume compression ratio of 0.60. This result was reproduced from the optical spectra calculation where inter-band transition was observed also at 0.60 volume compression ratio. Hence we can establish that IMT in NiO occurred at a volume compression ratio of 0.60. Our result is closer to one of the results (0.65) predicted by Feng and Harrison (2004) who used the B3LYP hybrid functional. The LDA+U functional has been observed to be a

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better functional for the treatment of Mott insulators and highly correlated materials like NiO (Shick *et al*., 1999).

Furthermore, the transition pressure was obtained from the Murnaghan EOS in equation (4) by fitting in the obtained volume compression ratio of 0.60. The values of B_0 and B_0' used were 166.83 GPa and 4.0 GPa respectively (Da-He, 1991) and a theoretical transition pressure of 271 GPa was obtained. The discrepancy between our theoretical result and that of the only known experimental result (240 GPa) by Gavriliuk *et al.* (2012) could arise from the sensitivity of the exchange-correlation functional used in DFT. Also, there is the question if NiO will undergo phase transition before IMT will take place. Experimental result by Gavriliuk *et al.* (2012) and our result have shown that NiO will undergo IMT at a transition pressures of 240 GPa and 271 GPa respectively but Eto *et al.* (2000); Raja and Sadhna (2008) predicted that NiO will undergo phase transition from rocksalt (cubic) structure to cesium chloride (rhombohedral) structure at pressures of 318 GPa and 300 GPa respectively. Thus, we can infer therefore that NiO will undergo IMT before phase transition.

Conclusion:

The IMT point in terms of volume compression ratio and pressure has been investigated by employing the electronic structure and optical spectra calculations. We achieved this transition at a volume compression ratio of 0.60 from both calculations and at a pressure of 271 GPa. Our result also confirms that NiO will undergo IMT before phase transition can take place since NiO phase transition from rocksalt (cubic) structure to cesium chloride (rhombohedral) structure occurred at a higher pressure. However, this work should stimulate further theoretical and experimental studies since understanding the electronic structure of NiO is interesting due to its rich and intriguing physical properties.

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