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Optical Spectra Description of the Insulator-Metal Transition of Nickel Monoxide by Volume Compression

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Abstract

The electron energy loss spectra were used to determine the insulator-metal transition point of nickel monoxide by volume compression. The optical spectra are based on electronic structures which have been obtained using the density functional theory implemented in the MindLab 5 code that employed the local density approximation plus the Hubbard on-site Coulomb interaction parameter (LDA+U) functional. At increasing volume compression, we observed a sharp rise in the electron energy loss spectrum at 0.60 volume compression ratio indicating inter-band transition.

Keywords: Nickel monoxide, Volume compression ratio, Insulator-metal transition, Density functional theory, Optical spectra.

1. Introduction

Nickel monoxide (NiO) which is a member of the first row transition metal oxides possesses a unique variety of physical properties. The partially filled *3d* shells which energetically overlap with the oxygen *2p* and the nickel *4s* evoke an intricate interplay between lattice, orbital and spin degrees of freedom. NiO is a mott-type insulator with a Néel temperature (T_N) of about 250^0C, above which it has a cubic rocksalt structure. Despite having only partially filled *3d* shells, NiO is insulating above and as well as below T_N.

If the transition point of NiO is known, it can then be used industrially as a switch that closes an electrical contact when the set transition point has been reached. When this set transition point is detected, the switch works to open or close the circuit and 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,

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electrochromic display devices and transparent conductive electrodes as well as in parts of functional sensor layers in chemical sensors (Jandow, 2015). Attractive features of NiO includes excellent durability and electrochemical 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).

Mott (1956) predicted possible insulator-metal (IMT) in compressed NiO. Despite the suggestions of the metallic high pressure phase of NiO by de Boer and Verwey (1937), Mott and Peierls (1937), it was not known at what volume compression ratio the material will transform from being an insulator to being a metal. Numerous theoretical studies gave contradictory predictions regarding the nature and IMT point of NiO. Cohen *et al.* (1997) carried out density functional calculation on NiO and predicted magnetic collapse from high spin states to low spin states under high pressure with a second order phase transition. Feng and Harrison (2004) predicted a volume compression ratio of 0.65 for transition to occur from calculation using the B3LYP (Becke, 3-parameter, Lee-Yang-Parr) hybrid functional (Becke, 1993; Lee *et al.*, 1988), and also a volume compression ratio of 0.40 for transition to occur from calculation using the PWGGA (Perdew-Wang generalized gradient approximation) functional (Perdew and Wang, 1989).

Their results are conflicting (Gavriliuk *et al.*, 2012), thus leaving the subject matter open for further studies. Also, little or no attention has been paid to determine the IMT point of NiO from optical spectra calculation. In this paper, we intend to overcome this challenge by determining the volume compression ratio at which NiO will undergo IMT from optical spectra calculation.

2. Materials and Methods

The theoretical methodology used in this work is based on the density functional theory (DFT) within the LDA+U approach implemented in the MindLab 5 code. The DFT differs from the wave function based methodology by using the electron density as the central quantity and it is readily applied to solve a many-body problem. The calculation assumes NiO as an antiferromagnetic material with lattice constant of 7.926 a.u in the absence of distortion. The LDA+U functional is applied, which is a better functional for the treatment of Mott insulators and strongly correlated materials like NiO (Shick *et al.*, 1999). The Muffin-tin radii of Ni^{2+} and

O^{2-} ions are 2.179 a.u and 1.783 a.u respectively and the volume compression ratio is defined as V/V_0 where V is the compressed volume, V_0 is the volume of the material before compression.

Different volume compression ratios were used in performing the calculation to determine its effect on the optical spectra of NiO. The Coulombic potential binding the electron-hole 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 very large, leading to a collapse of the Coulombic potential bining the electrons. This is explained by the Hamiltonian in Equation (1).

$$H_{sys} = T + U(r), \tag{2.1}$$

where

$$T = -\frac{h}{2m_e}\sum_i \nabla_i^2 \tag{2.2}$$

and

$$U(r) = \frac{1}{2}\sum_{i,j}\frac{e^2}{|r_i - r_j|}\,. \tag{2.3}$$

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 i^{th} electron and r_j is the position of the j^{th} electron. At sufficiently increase in pressure due to volume compression, the electrons then possess maximum kinetic energy and have freedom to move around freely or they become delocalized, ionized in the process and thus leading to metallization.

3. Results and Discussion

The electron energy loss spectra of NiO were computed using the MindLab 5 code for different reduced volume or volume compression ratios ranging from 0.10 to 0.85 in steps of 0.05. This work was carried out with the assumption that:

i. Standard temperature was maintained throughout the duration of the work

ii. The compression was hydrostatic, meaning that the material retains its cubic shape throughout the compression process and only the volume changed.

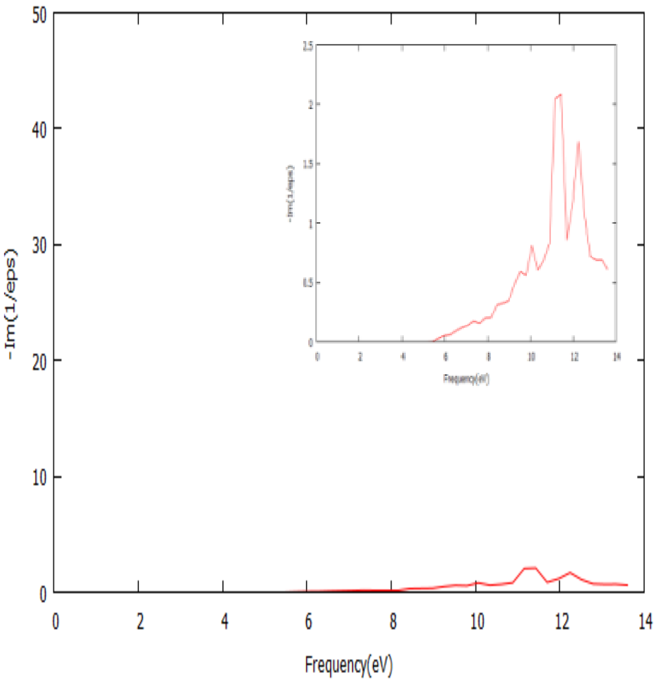

Fig. 1: Electron energy loss spectrum of NiO at 0.50 volume compression ratio. Inset shows enlarged region up to a value of 2.50 on the vertical axis.

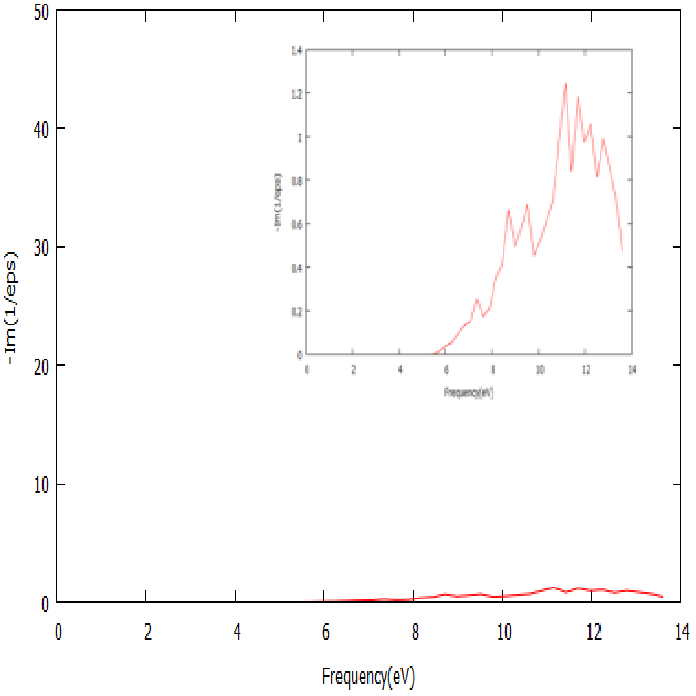

Fig. 2: Electron energy loss spectrum of NiO at 0.55 volume compression ratio. Inset shows enlarged region up to a value of 1.40 on the vertical axis.

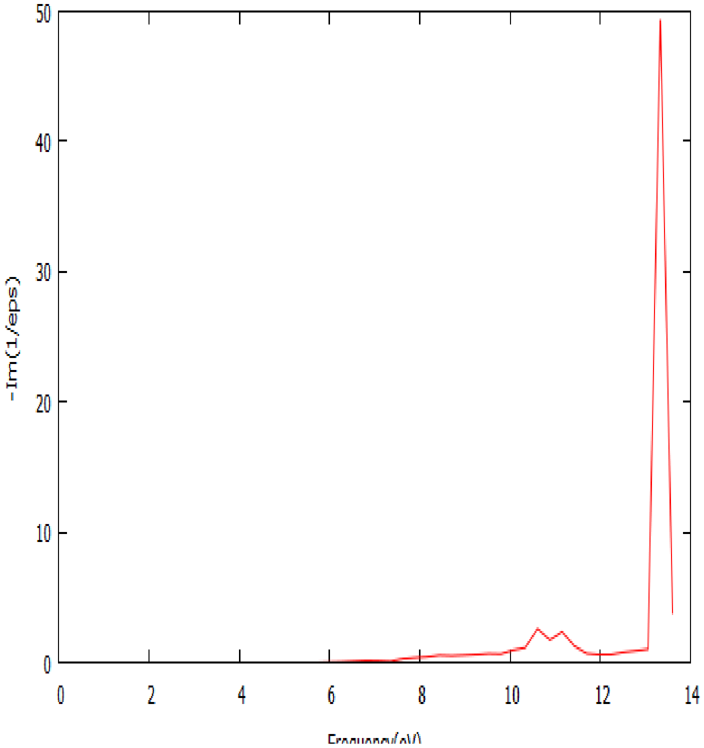

Fig. 3: Electron energy loss spectrum of NiO at 0.60 volume compression ratio.

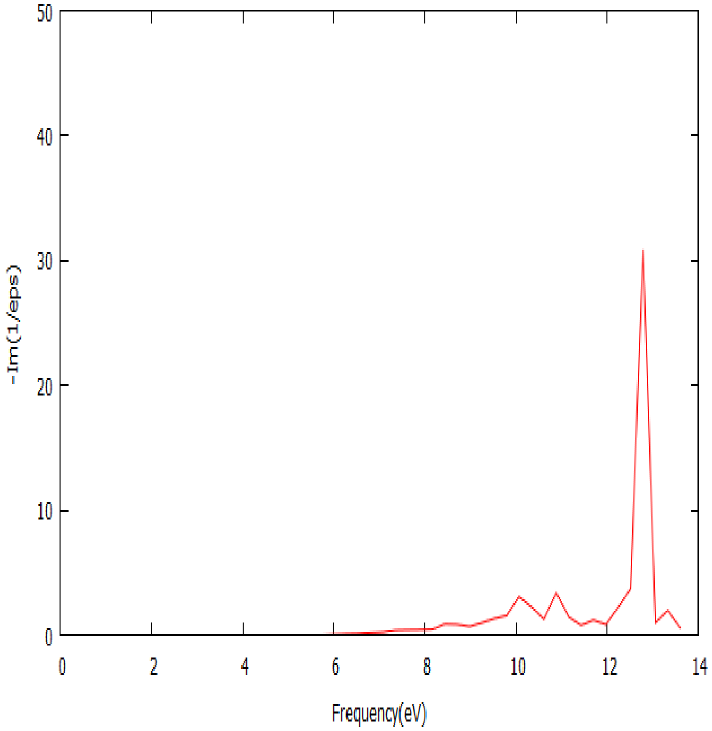

Fig. 4: Electron energy loss spectrum of NiO at 0.65 volume compression ratio.

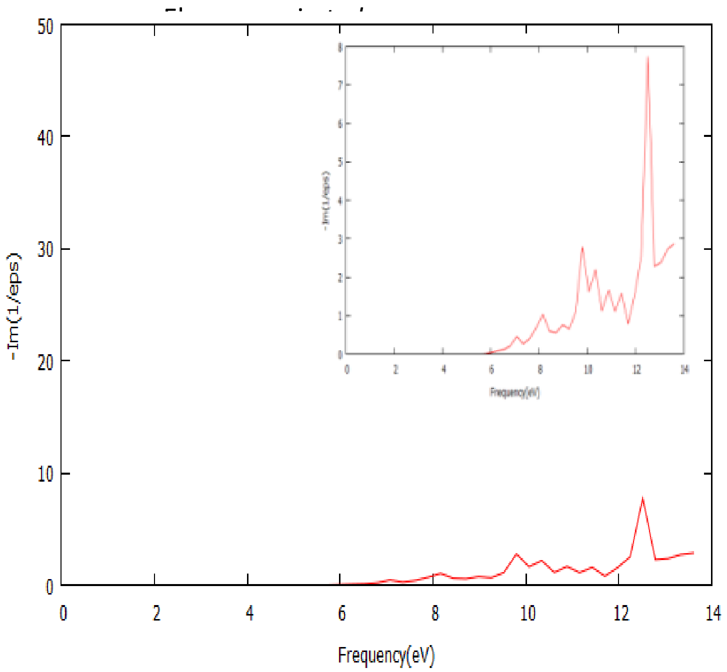

Fig. 5: Electron energy loss spectrum of NiO at 0.70 volume compression ratio. Inset shows enlarged region up to a value of 8.0 on the vertical axis.

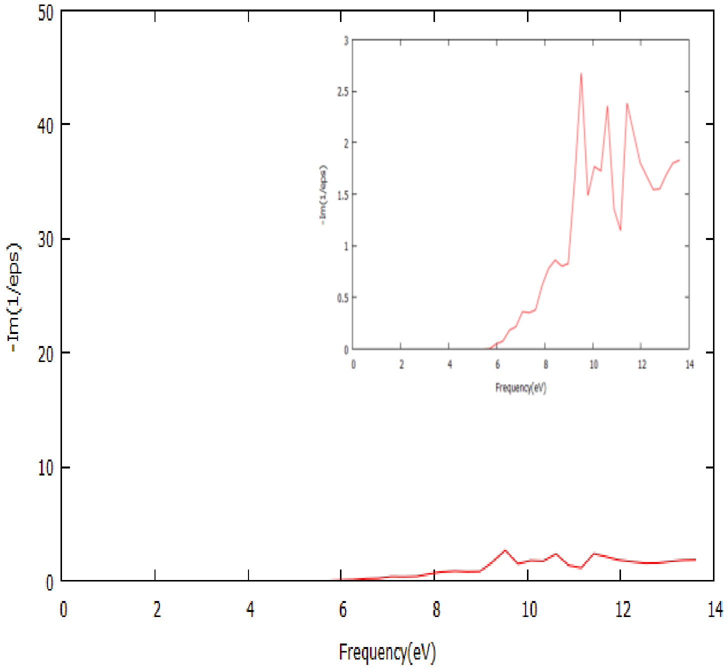

Fig. 6: Electron energy loss spectrum of NiO at 0.75 volume compression ratio. Inset shows enlarged region up to a value of 3.0 on the vertical axis.

The transition from the insulating state into the metallic state is predominantly from the O (*2p*) states to the Ni (*3d*) states. That is, electrons are transferred from the valence band which is primarily O (*2p*) character into the conduction band that is primarily Ni (*3d*) character. This charge transfer process is similar to the redox reactions (Waser *et al.*, 2009), and the resulting metallic Ni is responsible for the conduction.

Figure 1 and figure 2 show the electron energy loss spectrum of NiO at a volume compression of 0.50 and 0.55 respectively. The electron energy loss spectrum which is calculated from the imaginary part of the dielectric function, describes the movement or drift of electrons as they travel from one band to the other in the material. This drift of electrons can be observed from the waveform pattern (peaks) displayed in the electron energy loss spectra which is as a result of excitation of the electrons as pressure due to volume compression is being applied increasingly. However, at a volume compression ratio of 0.60, a sharp rise is observed in the electron energy loss spectrum. This is shown in Figure 3. This sharp rise is associated with inter-band transition which describes the energy loss of fast moving electrons traversing the material from one band to another (Mooradian and Fan, 1966; Adewale and Suleiman, 2010). This sharp rise observed at 0.60 volume compression started to drop as volume compression was increased further. This is illustrated in Figures 4, 5 and 6 respectively. The value of the volume compression ratio so obtained from this work is closer to one of the values (0.65) predicted by Feng and Harrison (2004) where they used the B3LYP hybrid functional. Our value is more exact because we employed the LDA+U functional which is a better functional for the treatment of Mott insulators and highly correlated materials like NiO (Shick *et al.*, 1999).

4. Conclusion

In summary, we have studied the IMT point of NiO at different volume compression ratios by employing optical spectra calculation and using the MindLab 5 code that has the DFT implemented in it. It was observed that as pressure due to volume compression was increasing, there was drift of electrons as seen from the waveform pattern in the electron energy loss spectra. A sharp rise in the electron energy loss spectra was observed at a volume compression ratio of 0.60 indicating inter-band transition. Thus, predicting that IMT in NiO will take place at a volume compression ratio of 0.60.

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