

Effect of Coulomb interaction on the band gap of NiO

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Abstract

The band theory and local density approximation LDA predict NiO to be a metal but experimentally this material is known to be an insulator. To overcome this problem, we employ the LDA+U (where U is the on-site Coulomb interaction) technique in order to get the true nature of the material. We observed an increase in the band gap of the material as we gradually increase the value of U. Our result was compared with other works and that of experimental result.

Keywords: LDA+U; Electronic band gap; on-site Coulomb interaction

1. Introduction

One of the transition-metal monoxides (TMOs) known as nickelmonoxide (NiO) which shows an antiferromagnetic (AFM) ordering (Engel and Schmid 2009 & Wei and Qi 1994) below its Neel temperature (Roth 1958; Rodl and Bechstedt 2012) has been discussed intensively for many years (Kunes et al 2007; Anisimov et al 1993; Mattheiss 1972; Norman 1991; Anisimov 1997 & Szotek et al 1993). This compound is known to crystallize in rocksalt structure in the paramagnetic phase (Rodl and Bechstedt 2012; Mattheiss 1972 & Schron et al 2010) and was thought to be an example of prototypical Mott insulator (Terakura et al 1984 and Brandow 1977) since the Hubbard U is responsible for splitting of the gaps, while other researchers argue that the compound is a charge transfer insulator (Wei and Qi 1994, Kunes et al 2007 & Zaanen 1985). Many years back, this compound was predicted to be a metal by theorist with the help of band theory (Terakura et al 1984 & Ren et al 2006) but experimentally is known to be an insulator (Hufner et al 1984; Sawatzky and Allen 1984). Boer and Verwey (1937) were the first to point out why the ground state property of NiO could not be described by the band theory but the basic concept explaining why materials such as NiO are insulators was formulated by Mott some decades ago (Mott 1949). In recent development, attempts have been made theoretically to calculate the energy gap of NiO in order to establish the well-known fact that NiO is an antiferromagnetic insulator. One of the commonly used techniques is the local spin density approximation (LSDA) (Fillippetti and Spaldin 2003; Leung et al 1991 & Mazin 1993) within the density functional theory (DFT). This approach is known to provide a reliable description of the ground state properties and electronic structure of solids. Despite the success of this approach, it could not account for the ground state properties of some materials especially those containing partially filled valence *d* or *f* shells known as strongly correlated materials in condensed matter physics (Kunes et al 2007; Szotek et al 1993 & Alfredsson et al 2004). One of the ways to overcome this challenge is to include the Mott Hubbard parameter U (Rodl et al 2009), the well-known LDA+U (Anisimov et al 1991). Although, the LDA+U has been used by several researchers to study the electronic structure (Anisimov et al 1997 & Bengone et al 2000), electron energy loss spectra (Dobysheva et al 2004) and dielectric constant of NiO (Lu-Hui et al 2013), much have not been said on the effect of gradual increase of the Hubbard U on the band gap of NiO. Some researcher have pointed out in their work that at some certain intermediate values of the on-site Coulomb interaction, properties such as the dielectric function (Bengone et al 2000), lattice parameter and the measured electron energy loss spectra (Dudarev et al 1998) have been calculated to be in better agreement with experimental results. In this work, we have not only calculated the electronic band gap of NiO in order to agree with experimental result but also to see the effect of gradually adjusting the on-site Coulomb interaction on the band gap of NiO thereby causing a metal-insulator transition as stated in (Mott 1968).

This paper is organised as follows: in Section II, we summarise the method and computational details. The electronic band structure and density of state (DOS) of NiO are discussed briefly in Section III. In Sec IV, a brief summary and conclusion is given.

2. Computational Details

All computations based on the LDA and LDA+U within the DFT approach have been performed using the MstudioMindlab 5.0 code (<http://www.physics.>) developed by (Savrasov 1996). In the calculations performed here, we have taken the lattice constant of NiO to be 7.926a.u. in the absence of distortion. Since the material is highly correlated, the correlation effect is treated and the double counting term has to be taken into account and the most common choice is the $U(n-1/2)$. The muffin tin sphere for Ni and O atoms are 2.179a.u and 1.783a.u respectively. During the self-consistent calculation, a full potential linear muffin tin orbital (FP-LMTO) working with plane wave representation is used. The k-integration technique is based on the tetrahedron method. In our calculation, U and J represent Coulomb and Exchange interaction and are defined by $U (=F^0)$ and $J = (F^2 + F^4)/14$ where F^0 , F^2 , and F^4 are the Slater integrals (Slater 1960) for 3d materials. The LDA functional used is that of (Vosko et al. 1980).

3. Results and Discussion

The band structure and DOS resulting from the LDA approach are shown in Figs. 1 and 2 respectively. We can see that the LDA gives small band gap of the order of 0.6eV. When compared to experimental result, the band gap got is far too small. This big difference is due to the fact that the LDA does not sufficiently localise the *d* electrons in this compound (Tran et al 2006). To overcome this problem, the on-site Coulomb interaction is introduced that is the LDA+U approach. We gradually introduce on-site Coulomb interaction by increasing the value of $F^0(=U)$ and keeping the exchange interaction constant. We observed an increase in the gap which is shown in Fig.3.

The maximum gap obtained is shown in Fig.4 and its corresponding DOS is shown in Fig. 5. Although the band gap does not give the experimental result, it is closer to experimental result than other approach as shown in Table 1. The value of the band gap got shows that NiO is an insulator as found by experimentalist (Hufner et al 1984; Sawatzky & Allen 1984). This gradual increase of the gap of NiO with increase in U can be seen to cause a phase transition from metal to insulator which was also observed by (Xiao-Bing and Harrison 2004). With this transition it is clear that the reverse process can take place experimentally since naturally, NiO is an insulator. So gradually decreasing U can cause an insulator-metal transition. This transition was observed experimentally by Ohta and co-workers by applying pressure (Ohta et al 2012). Although the band gap is significantly underestimated when compared to experimental result, it gave an insulating state. The reason for this is that U alone is not enough to give the desired gap. Unless the charge transfer energy is included (based on the fact that NiO is a charge transfer insulator) and given a value greater than that of U, the experimental result might not be achieved.

4. Conclusion

In summary, we computed the electronic band structure of NiO using the LDA and LDA+U techniques in order to determine the band gap of NiO. The gap from LDA gives a semiconductor while the LDA+U approach gives an insulator. We see from the Figs. 1 and 2 that at $U=0$, i.e. LDA, the metallic state is not achieved and this tells us that the reduction of U might not be sufficient except the introduction of other parameters like temperature or pressure in order to achieve metallic state.

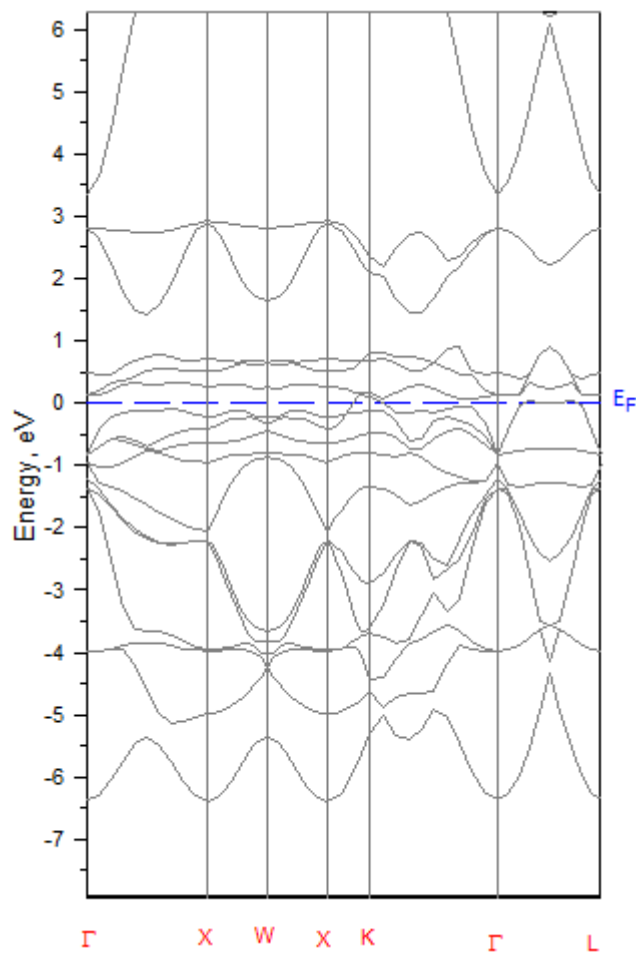


Fig. 1. Band structure of NiO in the absence of correlation with a band gap of 0.6eV.

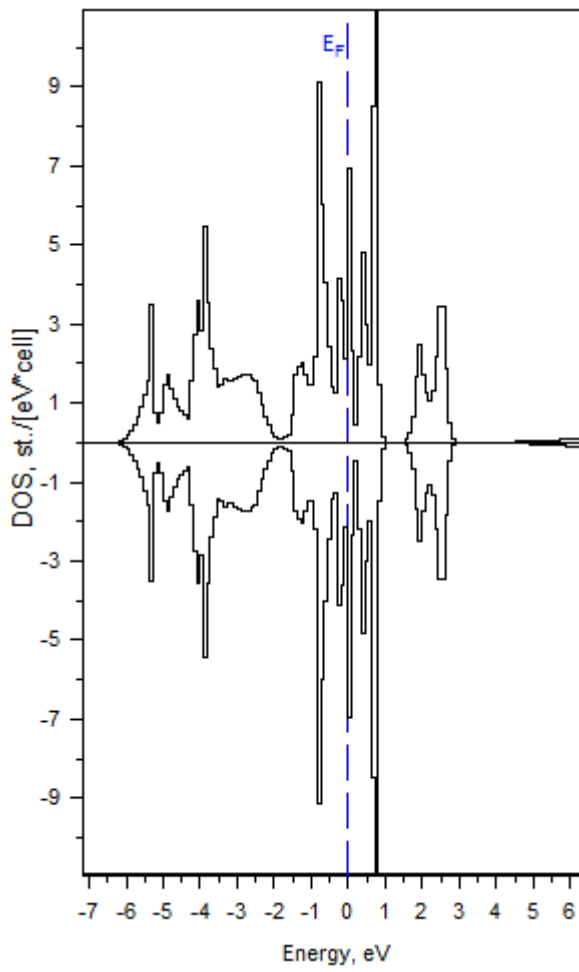


Fig. 2. DOS of NiO in the absence of correlation.

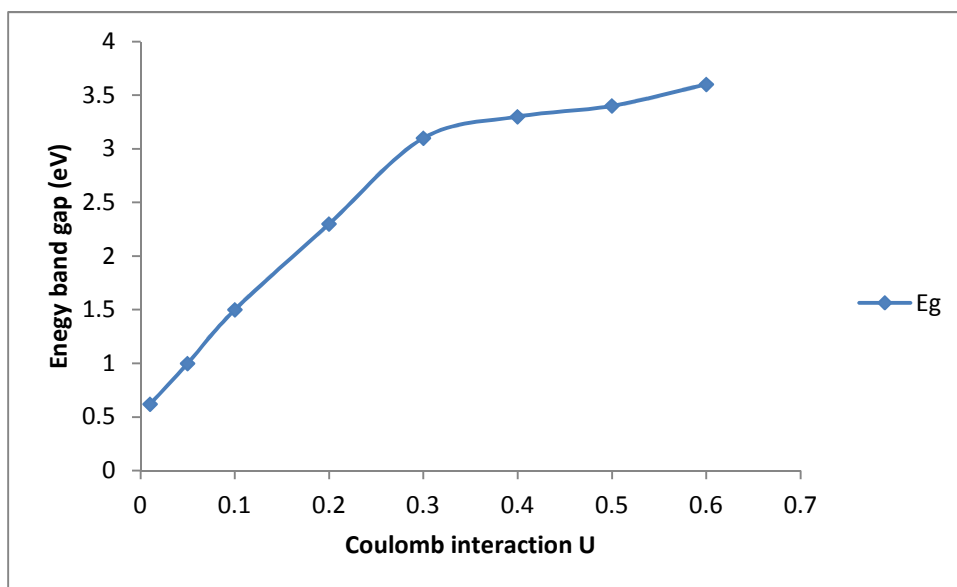


Fig. 3. Band gap of NiO plotted against U.

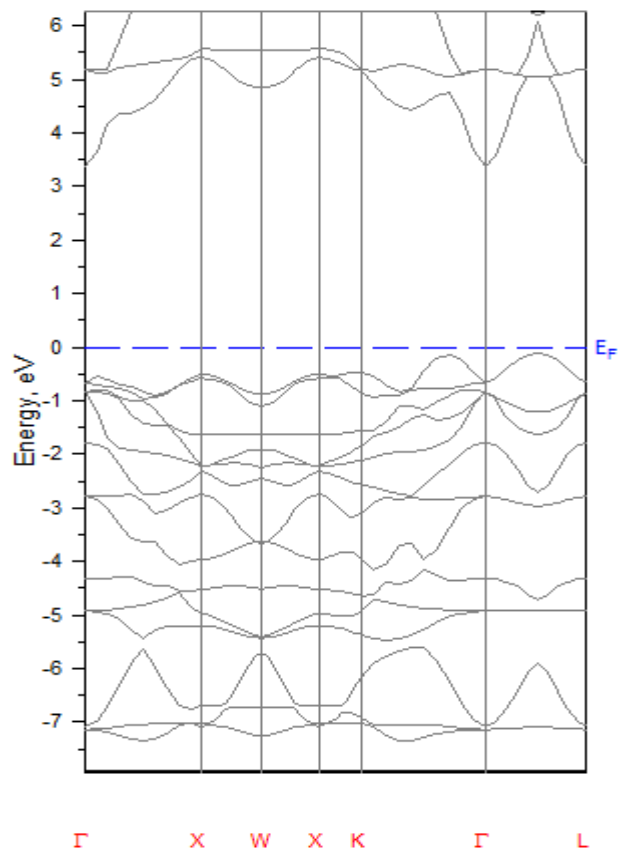


Fig. 4. Band structure of NiO with LDA+U calculation with a band gap of 3.6eV.

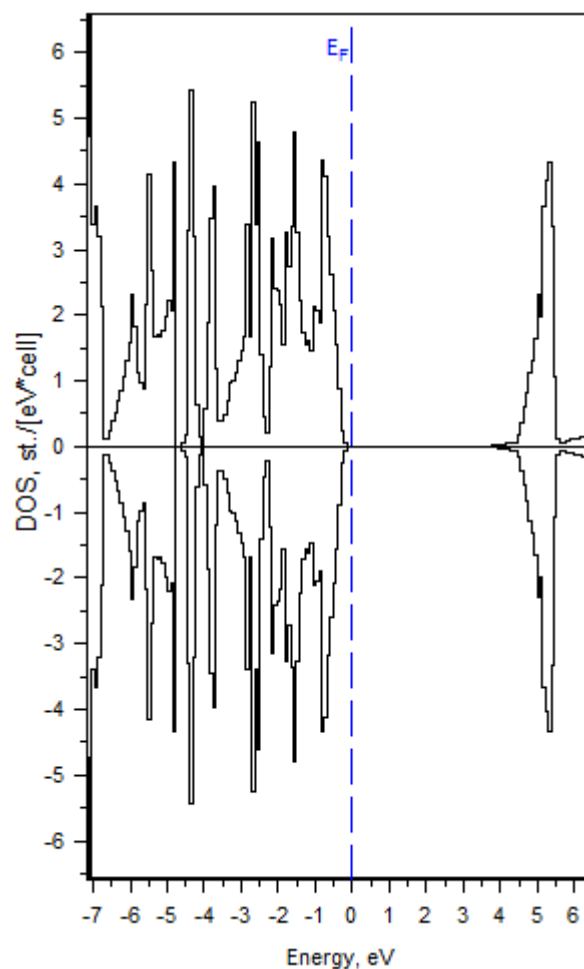


Fig. 5. DOS of NiO with LDA+U calculation.

Table 1. Electronic band gap of NiO from experiment (exp), Exact exchange (Exx), Localized density approximation including Coulomb interaction (LDA+U), band gap (E_g), Hybrid scheme and self-interaction corrected (SIC) LDA

compound	exp (eV)	Exx (eV)	LDA+U (eV)	E_g (eV)	Hybrid (eV)	SIC (eV)	This work (eV)
NiO	4.0 ^a 4.3 ^b	4.1 ^c	3.1 ^d	3.2 ^e	3.0 ^e	2.66 ^c	3.6

^aRef. (Hufner et al 1984), ^bRef. (Sawatzky and Allen 1984), ^cRef. (Engel and Schmid 2009 & Wei and Qi 1994) (
^dRef.(Anisimov et al 1991), and ^eRef.(Tran et al 2006).

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