Available online at www.sciencedirect.com

SCIENCE DIRECT®

Nuclear Instruments and Methods in Physics Research B 199 (2003) 406–410

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Photoelectron spectroscopy study on Li substituted NiO using PES beamline installed on Indus-1

A. Banerjee, S.M. Chaudhari *, D.M. Phase, B.A. Dasannacharya

Inter University Consortium for DAE Facilities, Khandwa Road, University Campus, Indore 452 017, India

Abstract

Photoelectron spectroscopy beamline based on a toroidal grating monochromator (TGM) is recently commissioned on Indus-1 storage ring. It has been used to carry out valence band photoemission study of Li substituted NiO. In this paper initially a brief description of the beamline components and the experimental station for angle integrated photoemission experiment is presented. The later part of this paper is devoted to studies carried out on $Li_xNi_{1-x}O$ with $x = 0.0$, 0.35 and 0.5 samples. Thin pellets of polycrystalline samples were used for the measurements reported here. Valence band spectra recorded on polycrystalline $Li_xNi_{1-x}O$ samples show drastic changes in various features as compared to that of pure NiO. The prominent changes are: (i) change in the relative contributions of Ni-3d and O-2p emissions, (ii) change in the peak position of Ni-3d from the top of the valance band of NiO and (iii) no noticeable change in the Ni satellite peak. These results are evaluated in terms of earlier findings in pure and low Li doped NiO.

PACS: 07.85.Q; 71.15.A

Keywords: Synchrotron radiation; Photoelectron spectroscopy; Li doped NiO; Beamline

1. Introduction

Taking into consideration requirements of the Indian user community and the most abundant photon flux available from Indus-1, it was decided to design and construct a beamline in the energy range of 10–200 eV as well as a corresponding photoelectron spectrometer. In this energy region, the choice of monochromator is mainly restricted to: (i) spherical grating monochromator; (ii) plane grating monochromator and (iii) toroidal grating monochromator. Even with this limited choice, the number of different optical configuration of beamlines that have been used is still large. The selection of particular optical arrangement for a beamline primarily depends on the application for which beamline is intended. For photoelectron spectroscopy study of the solids, the basic requirements are good photon flux at the sample and moderate resolution. Toroidal grating monochromator (TGM) fulfils both these requirements very well. In addition a single motion of the grating is required to scan the wavelength. Looking at these

---

* Corresponding author. Tel.: +91-731-463913; fax: +91-731-462294.

E-mail address: smc@iucindore.ernet.in (S.M. Chaudhari).

0168-583X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0168-583X(02)01584-7

advantages, a TGM based beamline for photoelectron spectroscopy study has been designed [1] for use on Indus-1 synchrotron source which is a 450 MeV electron storage ring [2]. The assembled beamline along with its workstation has been commissioned at one of the bending magnet ports of Indus-1. After commissioning the beamline first valence band and core level spectra of Ag and Pt were recorded successfully on 9 November 2000. Several experiments were then performed on different samples using this beamline to test the performance of the beamline [3].

Recently, using this beamline we have carried out valence band (VB) spectroscopic studies on Li substituted NiO in order to investigate modifications to the VB due to the substantial substitution of Li (35% and 50%) at Ni site. Interest in this type of substitution arise from the fact that we have carried out extensive investigation on this system to resolve the controversy related to structure and magnetism [4,5]. Apart from this, considerable efforts are given by various groups in the recent years to understand intriguing physical properties in this series of materials [6] which has technological importance as well in terms of Li batteries. These physical properties and the resulting concepts are closely related to the nature of the valence band. Earlier electron spectroscopic studies has shown that NiO is a charge transfer insulator and Li substitution ($\geqslant 2\%$) pin the fermi energy [7,8]. In addition to this, X-ray absorption studies has indicated that Li substitution creates hole in O-2p and not in Ni-3d maintaining the charge transfer characteristics [8]. However, to the best of our knowledge valence band study of Li substituted (Li $\geqslant$ 35%) NiO is not reported in the literature. In this context, our interest is to verify whether the conclusion drawn for valence band in low Li ($\leqslant 20\%$) doped NiO [9] can be extended to the highly Li ($\geqslant 0.35$) doped NiO samples. The energy range of present beamline is suitable to carry out the proposed study.

In this paper, we describe the main elements of the beamline in first section and then the results related to valence band spectroscopic studies carried out on $Li_xNi_{1-x}O$ samples with $x = 0.0$, 0.35 and 0.5 using this beamline are presented in Section 2.

2. Beamline description

The optical design of the beamline has been discussed earlier [1,3] and an outline is given here. The beamline consist of a pre-mirror to focus the incident radiation, a monochromator to select the wavelength of interest and a post-mirror to focus the monochromatic beam onto the sample. Various physical constraints such as the length of front end, shielding wall thickness, etc. restrict the placement of first mirror to 4 m from the tangent point. This mirror, which is toroidal in shape, accepts radiation over a horizontal acceptance angle of 10 mrad and a vertical acceptance angle of 2.5 mrad. The angle of incidence at the mirror is around 4.5° giving a deviation of 9° after reflection. The reflected beam is brought to focus at a distance of 2 m from the centre of the mirror where an entrance slit is located. The pre-mirror illuminates the entrance slit by 2:1 demagnification of the source. The toroidal grating monochromator (Jobin Yvon) has a three gratings (size 90 mm × 30 mm) and it operates at constant vertical deviation of 162°. Three gratings having groove density 1800, 600 and 200 are used to cover wavelength from ranges 60–180, 180–540 and 540–1600 Å, respectively. The gratings can be brought into working position without breaking the vacuum, and can be scanned in the position around a vertical axis passing through the grating. The monochromatic light is focused on an exit slit kept at 2636 mm from the grating centre. The beam aperture is mounted in the entrance arm of the monochromator chamber before the grating chamber to avoid reflected stray light reaching the optical components and hence ultimately to the sample. The entrance and exit slit assemblies are located at foci of the pre-mirror and TGM, respectively. Both the slits are identical and have horizontal as well as vertical adjustment. In vertical direction motions are continuous from 0 to 1 mm whereas in horizontal direction the slits height is adjustable in four discrete steps viz. 0.4, 0.8, 1.5 and 3 mm. The beam passing through the exit slit falls onto the post-mirror, which is also toroidal in shape. This mirror is kept at a distance of 990 mm from the exit slit and at a same distance from post-mirror a sample in experimental

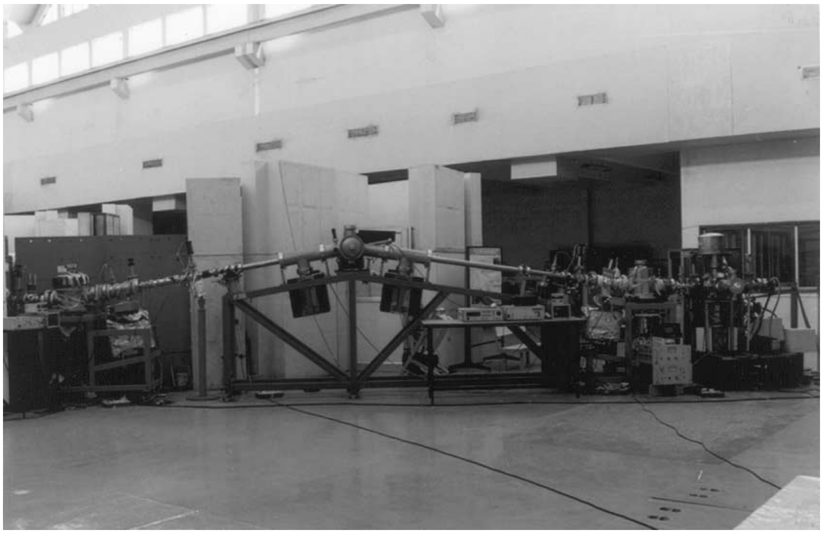

Fig. 1. Photograph of complete beamline installed on Indus-1 storage ring.

chamber is located. The deviation produced by post-mirror is 9° so that the beam striking the sample is parallel to the beam emanating from the source. Post-mirror produces a magnification of unity with the result that the spot size of the final image on the sample is a replica of the exit slit. Both the mirror chambers along with mirror mount system are fabricated indigenously. The details of this mirror mount system and chamber are described elsewhere [10].

To avoid contamination of the optical components and to make beamline compatible with the storage ring the base pressure in the entire beamline is kept better than 1×10^{-9} mbar. A combination of sputter ion pump and turbo pump backed with scroll pump at appropriate locations along the length of beamline are used to maintain the required vacuum.

The experimental station of this beamline is an angle integrated photoelectron spectrometer, which was designed and fabricated indigenously [3]. This consists of (1) 180° hemispherical analyser, (2) the experimental chamber with in situ heating and cooling arrangement of the sample mounted on XYZ sample manipulator, (3) sample preparation chamber equipped with quick load-lock magnetic sample transfer system, ion gun for controlled etching of the sample and diamond file type scraper; and (4) the associated electronics and the data acquisition system. A photograph of complete beamline installed on Indus-1 storage ring is shown in Fig. 1.

3. Valence band spectroscopy study on Li doped NiO

Samples used in the present investigation are prepared by solid-state route and characterized by Rietveld refinement of powder X-ray diffraction data [4,5]. Thin pellets of polycrystalline NiO, $Li_{0.35}Ni_{0.65}O$ and $Li_{0.5}Ni_{0.5}O$ were used for the measurements reported here. Good electrical contact was ensured with grounded sample holder by silver paste. Samples were repeatedly scraped and spectra were recorded under ultra high vacuum condition. The spectra reported in this article are recorded at photon energy of 134 eV since highest photon flux is available at this energy with present beamline. Fig. 2(a) shows the experimental valence band spectrum of NiO. For comparison calculated total density of states (DOS) of NiO using LMTO calculations [11] is given in Fig. 2(b). It is clear from Fig. 2(a) and (b) that in measured spectrum of pure NiO there is no distinct separation in Ni-3d and O-2p emission as seen in calculated DOS

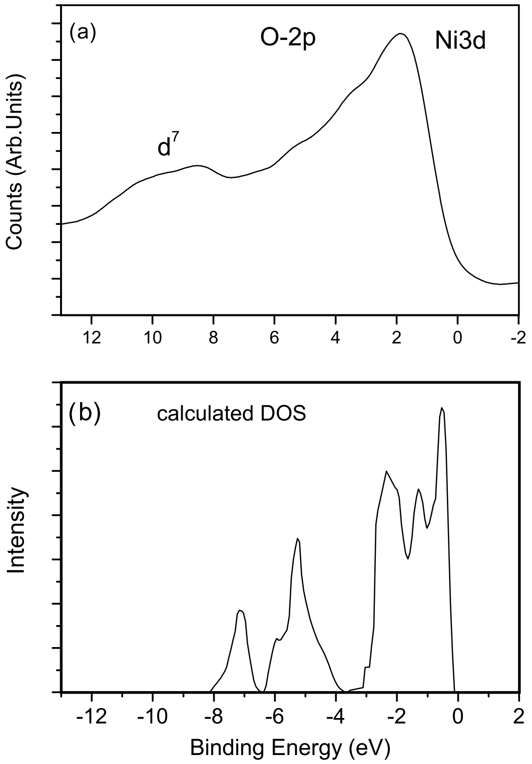

Fig. 2. (a) Measured valence band and (b) calculated DOS spectrum of pure NiO.

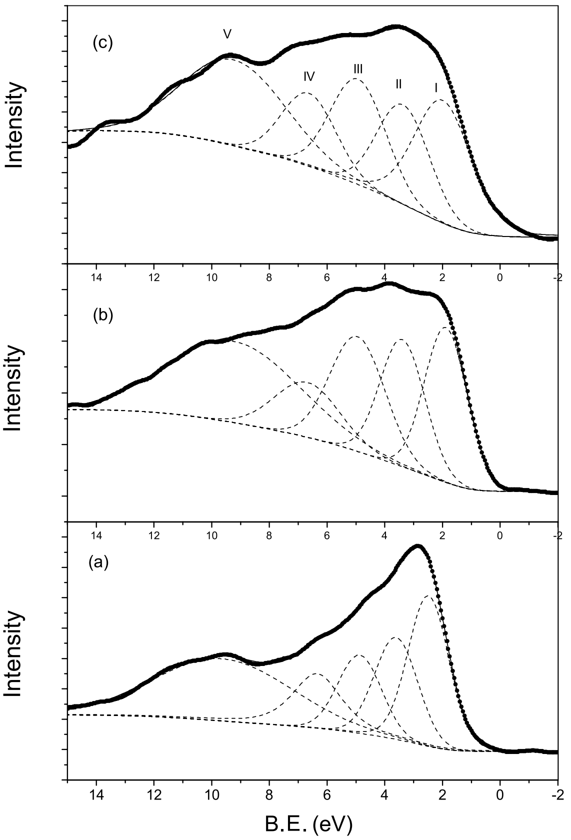

Fig. 3. Measured valence band spectrum of (a) pure NiO; (b) $Li_{0.35}Ni_{0.65}O$; (c) $Li_{0.5}Ni_{0.5}O$ samples.

spectrum. However, one can achieve good agreement between two spectra if one shift the 'd-part' of calculated DOS by about 1.5 eV to larger binding energy as reported by Hüfner [9]. This is used as a guideline for identification of structures in the measured spectrum. Moreover, experimental spectrum shows additional peak around 9 eV, which is due to Ni $3d^7$ satellite [12]. Calculated DOS spectrum does not show such satellite peak. It is known that single electron DOS calculation does not reveal satellite structure. If, on the other hand, one uses a cluster for the excitation spectrum of NiO, this calculation gives a $3d^7$ satellite at 9 eV below the Fermi energy [13]. The positions of O-2p and Ni-3d satellite peak in measured spectra were confirmed by varying the photon energy (40–70 eV) around the corresponding resonance conditions. These results are not shown here and will be reported elsewhere. Fig. 3 shows the experimental and fitted valence band spectra of pure and Li substituted NiO samples. Each spectrum clearly exhibits following three contributions. (1) The prominent structure in the observed spectrum with smallest binding energy is due to the Ni-3d emissions (Peaks I and II), (2) this is followed in binding energy by emission out of O-2p band (peaks III and IV), (3) the prominent feature about 9 eV below the top of Ni-3d emission is due to the Ni satellite peak (peak V). While fitting the spectra a pseudo-Voigt peak profile function is used. For pure NiO (Fig. 3(a)) respective peak positions matches well with reported data [7,9]. In this case, ratio of area under Ni-3d and O-2p peak is 1.6:1. This ratio has a significance only for estimating roughly the relative density of states and to compare the same with doped samples. The valence band photoemission spectra of $Li_{0.35}Ni_{0.65}O$ and

$Li_{0.5}Ni_{0.5}O$ are shown in Fig. 3(b) and (c), respectively. These spectra show clear difference from that of pure NiO case; however, overall features in the spectra of two heavily doped samples are similar as far as the peak positions are concerned. Though there are changes in intensity of O-2p peak, the fitted spectra for these two samples show that the ratio of area under the Ni-3d peak to that of O-2p peak is reduced to about 1.2:1. This shows that Li substitution even upto 50% has not reduced the Ni-(DOS)/O(DOS) in that proportion indicating that this substitution has created a substantial amount of holes in O-2p state confirming a charge transfer nature of the system. In addition to this the Ni (3d) peak positions have shifted towards lower binding energy by about 0.5 eV and there is no observable shift in O-2p part of the spectrum. This is in agreement with earlier studies carried out on low Li doped NiO samples [9]. It has been shown that the change in the various peak position and fermi energy gets saturated for Li doping beyond 2%.

Thus the present study shows that the conclusion drawn from various electron spectroscopy studies and X-ray absorption study on low Li doped samples are also valid for high Li doping. The observed shift of 0.5 eV in Ni-3d peak position may be attributed to the metallic character given to nickel by Li doping. This is also corroborated by our earlier work on conductivity measurement on these samples [5] showing reduction in average band gap.

4. Conclusions

In conclusion our measurement show that even with heavy doping of Li the O-2p and Ni-3d peak positions remain unchanged. Our analysis show that the Li doping creates hole in O-2p, confirming earlier conclusion drawn on low Li doped samples. These results clearly demonstrate the capability of present beamline to carry out good quality photoemission experiments.

Acknowledgements

The authors would like to specially thank the Indus-1 operating staff. Help rendered by Dr. A. Bajpai in sample preparation and Mr. A.D. Wadikar in beamline operation is gratefully acknowledged. We thank Prof. M.S. Hegde for fruitful discussions.

References

[1] S.M. Chaudhari, A.V. Pimpale, Nucl. Instr. and Meth. A 359 (1995) 274.
[2] S.S. Rammurthi, G. Singh, Nucl. Instr. and Meth. A 359 (1995) 15.
[3] S.M. Chaudhari, D.M. Phase, A.D. Wadikar, G.S. Ramesh, M.S. Hegde, B.A. Dasannacharya, Current Sci. 82 (2002) 101.
[4] A. Bajpai, A. Banerjee, Phys. Rev. B 55 (1997) 12439.
[5] A. Bajpai, A. Banerjee, Phys. Rev. B 62 (2000) 8996.
[6] F. Reynaud et al., Phys. Rev. Lett. 86 (2001) 3638.
[7] S. Hüfner, P. Steiner, F. Reinert, H. Schmitt, P. Sandl, Z. Phys. B 88 (1992) 247.
[8] P. Kuiper, G. Kruizinga, J. Ghijsen, G.A. Sawatzky, Phys. Rev. Lett. 62 (1989) 221;
G.A. Sawatzky, J.W. Allen, Phys. Rev. Lett. 53 (1984) 2339.
[9] S. Hüfner, Adv. Phys. 43 (1994) 183, and references therein.
[10] S.M. Chaudhari, D.M. Phase, G.R. Kulakarni, A.V. Pimpale, in: A.K. Sinha, N. Venkatramani (Eds.), Proceedings of the International Conference on Vacuum Science and SRS Technology (INCOVAST), India, Vol. 1, 1995, p. 283.
[11] O. Jepson, O.K. Anderson, Z. Phys. B 97 (1995) 35.
[12] S. Hüfner, F. Hullinger, J. Osterwalder, T. Riester, Solid State Commun. 50 (1984) 83.
[13] A. Fujimori, F. Minami, Phys. Rev. B 30 (1984) 957.