

# **dd excitations in three-dimensional $q$ -space: A nonresonant inelastic X-ray scattering study on NiO**

N. HIRAOKA<sup>1(a)</sup>, M. SUZUKI<sup>2</sup>, K. D. TSUEI<sup>1</sup>, H. ISHII<sup>1</sup>, Y. Q. CAI<sup>3</sup>, M. W. HAVERKORT<sup>4</sup>,  
C. C. LEE<sup>5</sup> and W. KU<sup>6</sup>

<sup>1</sup> National Synchrotron Radiation Research Center (NSRRC) - Hsinchu 30076, Taiwan

<sup>2</sup> Japan Synchrotron Radiation Research Institute (JASRI) - Kouto 1-1-1, Sayo, Hyogo 679-5198, Japan

<sup>3</sup> National Synchrotron Light Source II, Brookhaven National Laboratory - Upton, NY 11973, USA

<sup>4</sup> Max Planck Institute Stuttgart - Heisenbergstrasse 1, 70569 Stuttgart, Germany, EU

<sup>5</sup> Institute of Physics, Academia Sinica - Nankang, Taipei 11529, Taiwan

<sup>6</sup> Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory Upton, NY 11973, USA

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**Abstract** – We have studied the  $dd$  excitations in NiO over three-dimensional momentum ( $q$ ) space using nonresonant inelastic X-ray scattering. In addition to the previously reported peaks at 1.7 and 3.0 eV, another peak is found at 1.0 eV, with a dramatically different intensity distribution in momentum space. Contrary to the other two peaks that form oval structures maximizing at [111] directions, the 1.0 eV peak displays appreciable intensity along low-symmetry axes near [311] and [210], but vanishes in the three principal axes [100], [110], and [111], indicating a significant difference in the exciton wave function. We find good agreement between the experimental data and two state-of-the-art theories, advocating investigating other strongly correlated materials with similar experimental/theoretical approaches.



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As prototypes of strongly correlated systems, the transition metal oxides having the simple NaCl-type structure offer a fertile ground for various experimental and theoretical investigations. Investigation of their electronic structure, for examples the so-called Zhang-Rice singlet in the cuprates and its relationship with the Hubbard bands across the Mott gap, has been one of the major topics of the field [1–9]. Understandably, the atomic scale local  $dd$  excitations within the Mott gap has recently raised considerable interests [10–19], as they provide the building block for the low-energy electronic structure of the crystal. Particularly, a recent demonstration of the strong  $q$ -dependence in the intensity of nonresonant inelastic X-ray scattering (NIXS) and the related  $q$ -selection rule [14] has advocated this technique as a direct and powerful tool for the challenging task of studying such local excitations.

Specifically, the  $dd$  excitations are intra-atomic transitions among  $d$  electrons of even parity, and thus there are few experimental techniques capable of measuring them directly. For example, they have little intensity in optical experiments [20], and thus they are easily masked by excitations due to impurities or defects. Resonant inelastic X-ray scattering (RIXS) at the transition metal  $K$ -edge with hard X-rays only modestly enhances their intensity because of the spherical symmetry of the core-hole wavefunction of the  $K$ -shell. Soft X-ray RIXS at the  $L$ - or  $M$ -edges on the other hand provides a large enhancement. However, in addition to the limited  $q$ -range, the indirect transition process through an intermediate state makes it difficult to capture the essential nature of the excitations. Therefore it is remarkable that the  $dd$  excitations, having low intensity at low  $q$  ( $< 3\text{\AA}^{-1}$ ), exhibit strong intensity at high  $q$  in the NIXS experiments, due to the breakdown of the dipole selection rule and also to a better matching of the momentum transfer to the size of the local excitations. It is noted that electron energy loss spectroscopy (EELS)

<sup>(a)</sup>E-mail: hiraoka@spring8.or.jp

provides equivalent information as NIXS at low  $q$  [21–25]. However, EELS intensity rapidly drops as  $q$  increases and the technique is often limited in the high  $q$ -range due to multiple scattering.

The observation of the strong  $q$ -dependence of the  $dd$  excitations in NIXS experiments [14] prompted detailed theoretical investigations based on both a local many-body approach on a cluster [15] and the time-dependent density functional theory (TDDFT) implemented with the LDA+U functional (TDLDA+U) [19]. The former is advantageous in describing local interactions such as the multiplet structure of the Coulomb vertex and spin-orbit coupling while the latter is a novel approach based on the first principles, aiming to reproduce a total NIXS spectrum including charge transfer excitations and collective excitations occurring over large  $r$ -space as well as intra-atomic excitations. The results are summarized as follows. Three major peaks due to the  $dd$  excitations are observed at 1.0, 1.7 and 3.0 eV in NiO. The 1.7 and 3.0 eV features having  $T_{1g}$  symmetry exhibit strong intensities along the [111] axis at high  $q$  ( $\sim 7 \text{ \AA}^{-1}$ ). In contrast, the 1.0 eV feature having  $T_{2g}$  symmetry shows negligible intensities on high symmetry axes such as [100], [110], or [111] but appreciable intensity on low symmetry axes such as [311]. Their particular behavior is seen in the three-dimensional (3D)  $q$ -space representation by TDLDA+U in ref. [19]. While the TDLDA+U still has a limitation in producing the exact excitation energies, the cluster model relies on parameters to obtain the energies. Although the two theories appear to be essentially in agreement in terms of the angular dependence of the intensity, so far neither detailed comparison nor a critical examination with an experiment has been reported.

It is of central importance to clarify how faithfully these theories represent reality. The TDLDA+U theory has provided excitation energies only in qualitative agreement with the experiment. Naturally one should question how accurate the 3D representations of the TDLDA+U theory are. The cluster theory on the other hand involves various external parameters, which do not necessarily ensure a good description of the  $q$ -dependence. Nonetheless, there is a substantial lack of experimental data to examine these theories. For example, even the existence of the 1.0 eV peak has not yet been fully confirmed, and its  $q$ -dependence has not been investigated<sup>1</sup>. The cluster model predicts fine structures in each peak due to the spin-orbit and many-body interactions but this has not been examined. There is therefore an urgent need to examine these theories by experiments. Such experiments by NIXS however have been particularly challenging, as it requires an energy resolution sufficiently high to resolve the low-energy  $dd$  excitations, as well as sufficient

intensity to collect the data at many  $q$  points for the thorough examination.

In this article, we report on the first experimental 3D mapping of the intensity distributions of the  $dd$  excitations in NiO. We have observed all of the excitation features predicted by the theories in the spectra recorded using 190-meV resolution. Sampling at 120  $q$ -points with reasonable statistics reveals completely different types of topology in the intensity distributions in 3D  $q$ -space between the 1.0 eV feature ( $T_{2g}$  symmetry) and the 1.7 and 3.0 eV ones ( $T_{1g}$ ). They are rigorously compared with the two theories recently reported in exactly the same form. Since these theories have never been compared in a quantitative manner, this report also provides the first opportunity to see how consistent they are. Note that the calculation using Wannier functions (of TDLDA+U) has undergone a major revision, compared with that reported in the reference [14], and the revision results in a qualitatively different intensity distributions in 3D  $q$ -space [19]. Therefore, how this compares with an experiment and whether the theories are consistent with each other are still in question.

The experiments were performed at the Taiwan IXS beamline at SPring-8, Japan (BL12XU) [26]. The synchrotron radiation emitted from an undulator light source was monochromatized by a Si 111 double-crystal monochromator to a 1.4 eV energy width, and then the energy width was further reduced to  $\sim 140$  meV by a pair of Si 400 channel-cut crystals. The beam was focused by a Pt toroidal mirror into a  $\sim 80$  (vertical)  $\times 120$  (horizontal)  $\mu\text{m}^2$  spot, which irradiated a NiO sample obtained from a commercial source. The scattered X-rays are monochromatized by three spherical Si 555 diced analyzers ( $R = 2$  m) that were positioned along the vertical axis to the scattering plane. Finally they were counted by a Si diode detector. IXS spectra were recorded by scanning the incident photon energy ( $E$ ) while the scattered photon energy ( $E_o$ ) was fixed at 9890 eV. The energy range 0.4–3.6 eV was scanned with a total resolution of  $\sim 190$  meV. Compared with our highest intensity set-up (1.4 eV resolution), a substantial amount of intensity was lost and the relative intensity was only several percent. Nevertheless, such a resolution was essential to resolve the 1.0 eV feature from a tail of the strong elastic line. Due to the Thomson scattering pre-factor, NIXS has a node in the scattering cross-section at a scattering angle of  $90^\circ$  (corresponding to  $\sim 7 \text{ \AA}^{-1}$  at 10 keV) if the polarization vector of the incident beam is in the horizontal scattering plane. To avoid this node, the polarization vector, being originally horizontal, was rotated to vertical using a 0.5 mm thick diamond crystal, which worked as an X-ray half-wave plate used in the 220 Laue geometry [27,28]. We obtained the linear polarization of  $P_L = (I_h - I_v)/(I_h + I_v) = -0.85$ , where  $I_h$  ( $I_v$ ) denotes the intensity of the horizontal (vertical) polarization component.

Figure 1(A) shows the directions along which the spectra were measured. Eight spectra per axis were collected along 15 axes in the irreducible wedge of the cubic crystal

<sup>1</sup>The 1.0 eV peak was observed by several resonant experiments [17,18] but such a strong anisotropy was not observed because other transition channels govern the resonant case. We focus our discussion on the non-resonant case, in which the strong anisotropy is observed.

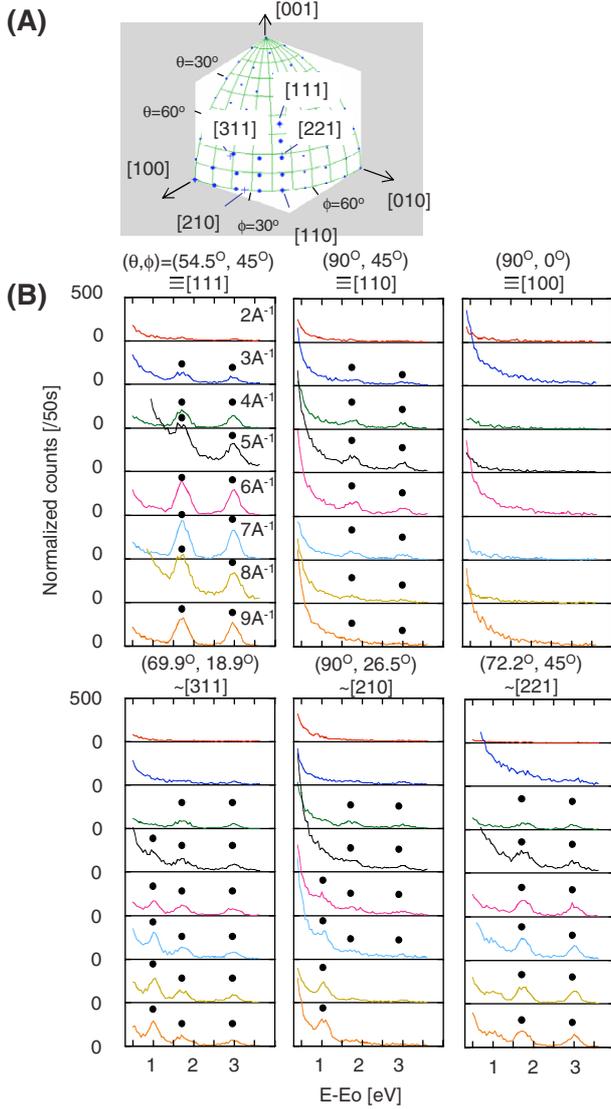


Fig. 1: (Color online) (A) 3D plot of the axes along which IXS spectra were measured (15 axes): Eight spectra were (nominally) measured at  $q=2-9 \text{ \AA}^{-1}$  with a  $1 \text{ \AA}^{-1}$  step per axis. The measured axes are shown by the larger circles while the smaller circles are their equivalent axes in the cubic symmetry. (B) Examples of IXS spectra, measured with an overall resolution of 190 meV using  $\sim 9.9$  keV X-rays.

(total 120 spectra). We took approximately an hour to measure a spectrum and half a day to collect eight spectra along each axis including the sample alignment. The elastic scattering was very strong near Bragg spots in  $q$ -space and its large tail made it difficult to extract the features of the excitations. Therefore spectra near Bragg spots were measured with a small offset ( $\sim 0.3 \text{ \AA}^{-1}$ ) of the  $q$  vector. Finally the intensity maps were obtained using a linear interpolation. Figure 1(B) shows examples of the measured spectra. There are strong peaks at 1.7 and 3.0 eV at  $q \sim 7 \text{ \AA}^{-1}$  along the [111] axis. They are substantially weaker on [110] while they vanish on [100] as has previously been reported [14,15,19]. In addition

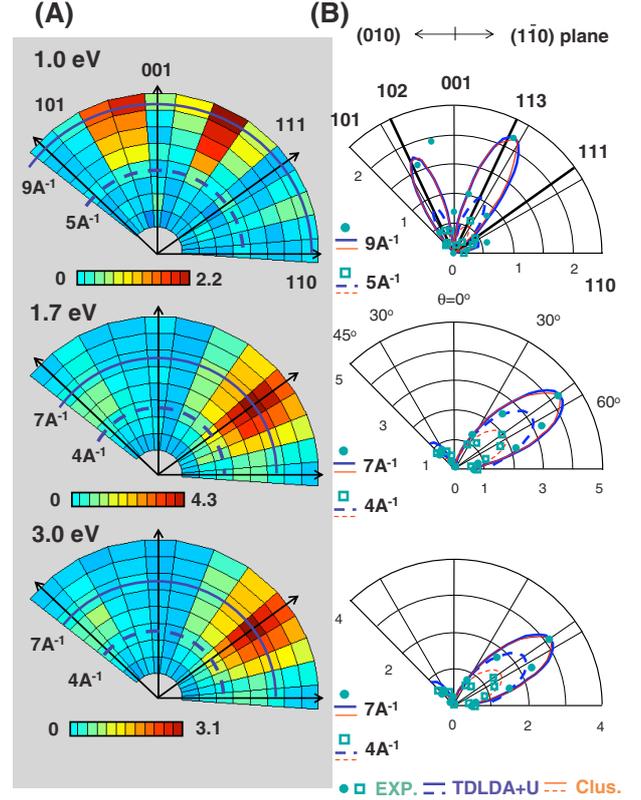


Fig. 2: (Color online) (A) Experimental intensity maps of 1.0, 1.7 and 3.0 eV features: each one consists of the maps on two planes,  $(1\bar{1}0)$  and  $(010)$ . (B) Polar plots along  $q=9$  or  $7 \text{ \AA}^{-1}$  (circles) and  $5$  or  $4 \text{ \AA}^{-1}$  (squares), compared with theories previously reported. Thin curves are of the cluster theory while thick ones are of TDLDA + U. Solid and broken curves are for  $q=9$  (or  $7$ ) and  $5$  (or  $4$ )  $\text{ \AA}^{-1}$ , respectively.

to these features, another peak is clearly seen at 1.0 eV along the axes near [311] and [210]. The 1.0 eV peak has a width of  $190 \pm 10$  meV, corresponding to the instrumental resolution. The other two peaks are slightly wider,  $260 \pm 10$  meV, implying the existence of multi peaks as predicted in ref. [15]. A higher resolution would be necessary in order to discuss the line profile in detail. At the present resolution, we found neither significant change in energy nor their line width throughout all the spectra.

In fig. 2(A) we present the 2D intensity maps of the  $dd$  excitations on the  $(1\bar{1}0)$  plane including the [001], [111], and [110] axes, and also the (010) plane which includes the [001] and [101] axes. The maps were obtained through a fitting analysis with four parameters, *i.e.*, the amplitudes of three Lorentzians for the excitation features and one for the tail of the elastic line. Figure 2(B) shows the polar plots of the intensity along  $|q|=9$  or  $7 \text{ \AA}^{-1}$  (indicated by circles) and along  $5$  or  $4 \text{ \AA}^{-1}$  (squares) for a comparison with the theories. The thick curves in fig. 2(B) indicate the intensity distributions predicted by TDLDA + U, while the thin curves denote those by cluster theory. Theoretical data are identical to those in the previous reports [15,19].

The exciton at lower energy in ref. [19] corresponds to the 1.0 eV peak ( $T_{2g}$ ) while the exciton at higher energy to the 1.7 eV and 3.0 eV peaks ( $T_{1g}$ ). They are rescaled so that the maximum intensity of each feature is the same as that of the experimental data. The agreement is markedly good: the 1.0 eV feature has its maximum near  $\theta = 30^\circ$  while the 1.7 and 3.0 eV features have maxima around  $\theta = 55^\circ$  ([111] axis). Nevertheless, several minor differences are found. First, the TDLDA + U overestimates at lower  $|q|$ , *i.e.*, 5 or  $4 \text{ \AA}^{-1}$ , indicating a slightly more delocalized orbitals, due to a well-known self-interaction problem of LDA-derived approximations. Second, there is a clear discrepancy in the intensity distribution of the 1.0 eV feature between the [001] and the [101]. Both theories predict strong intensity at  $\theta \sim 22.5^\circ$ , while the experiment shows strong intensity at  $\sim 18^\circ$ , which is closer to the [001]. This is due to a technical reason in the experiment as discussed in the next paragraph. Third, the experimental intensity distributions appear more concentrated than the theoretical ones around  $\theta = 55^\circ$  for the 1.7 and 3.0 eV peaks and at  $\theta = 30^\circ$  for the 1.0 eV peak. The reason is not clear. A possible explanation could be due to the statistical errors in the experiment. Indeed, the difference is only slightly larger than the error bars (approximately the same size as the circles) but this tendency is consistently seen for the three peaks. Another possibility is antiferromagnetic domains: namely, the X-ray beam could irradiate a few domains oriented along a specific axis if they were as large as the beam size. However, we saw little intensity variation across the Néel temperature (not shown), above which the domain size substantially decreases, suggesting the influence is minor. The reason that we believe to be most probable is more intrinsic: the real wave function of the exciton could be delocalized in  $r$ -space or be localized in  $q$ -space due to an interaction between adjacent  $d$ -atoms, which is omitted in both the theories. The examination is interesting but difficult at present, requiring further improvements of the theories.

The most prominent difference between the 1.0 eV feature and the 1.7 and 3.0 eV features is that the former has two regions of high intensity on the  $(1\bar{1}0)$  plane as well as the (010) plane, while the latter have only on the  $(1\bar{1}0)$  plane. This difference produces the intensity distributions of dramatically different topology in 3D  $q$ -space. Figure 3 displays the experimental intensity distributions of each excitation in 3D  $q$ -space along with those from the theories. These plots indicate high-intensity regions, showing intensities higher than 60% of the maximum for each excitation. The agreements between the experiment and the theories are excellent. The agreement with the TDLDA + U is remarkable, considering that the adiabatic approximation fails to split the high-energy exciton ( $T_{1g}$ ) into two peaks (as would all the existing adiabatic first-principles approximations [19].) In terms of the angular distribution, the agreement for the  $T_{1g}$  excitations is particularly excellent: both the experiment and the theories provide the oval structure pointing along the [111]

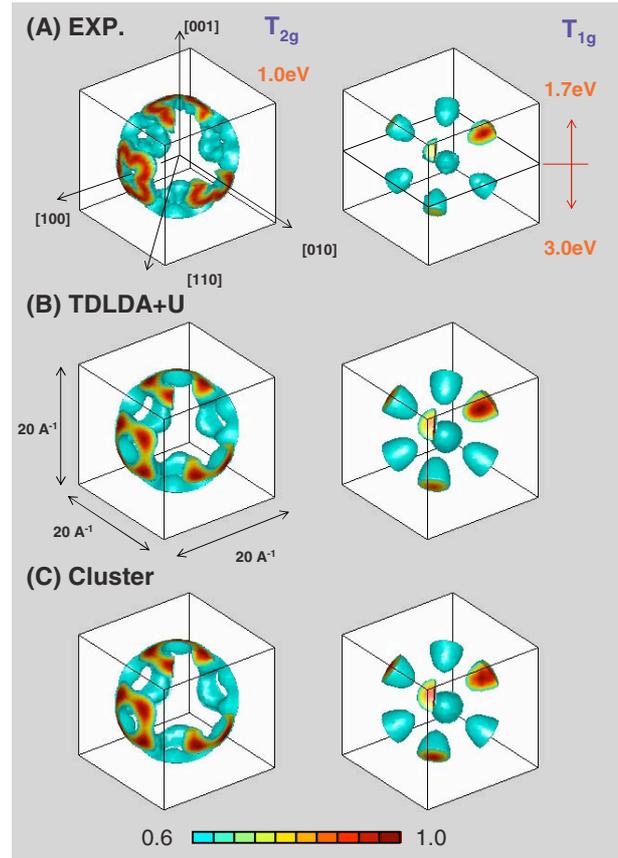


Fig. 3: (Color online) Intensity distributions of the  $dd$  excitations in 3D  $q$ -space in the experiment (A), those by the TDLDA + U theory (B) and by the cluster theory (C). They are normalized so that the maximum intensities are 1. Intense regions, higher than 60% of the maximum, are displayed. Right panel in (A) consists of the plot for the 1.7 eV peak (upper panel) and that for the 3.0 eV peak (lower panel), which are almost identical.

axis. The intensity distribution of the 1.0 eV excitations ( $T_{2g}$ ) in the experiment has a loop structure surrounding the [100] axis but the theories provide an inhomogeneous loop, in which the intensity is concentrated around the [311] axis. This difference arises from the multiple analyzers used in the experiment. The upper and the lower analyzers positioned out of the (001) plane by  $\pm 3$  degrees, deteriorating the  $q$  resolution. As a result, the most intense parts are inter-connected, making a homogeneous loop.

In summary, we have mapped out the intensity distributions of the  $dd$  excitations in NiO over 3D  $q$ -space using nonresonant IXS. An additional peak is found at 1.0 eV that has a significantly different distribution than those of the previously reported 1.7 and 3.0 eV peaks. The former has a loop structure surrounding the [100] axis while the latter oval structure pointing along the [111] axis. These behaviors agree remarkably well with those predicted by the cluster theory and TDLDA + U theory, indicating a good description of the theoretical wave functions. On the other hand, several minor differences are also found. Some

of them are simply explained by technical limitations such as a *q*-resolution of the experiment but it is unlikely that the narrower distribution of the intensity around [111] (or [311]) axis observed by the experiment is explained by such an extrinsic reason. An interaction between adjacent *d*-atoms is one of the possibilities. The examination would be interesting but it requires further major revisions of the theory. Regarding the excitation energies, the TDLDA + U theory needs more efforts to achieve a quantitative agreement while the cluster theory is required to provide the correct energies with parameters as few as possible. Finally, we suggest further investigations with a similar approach on other systems, *e.g.*, of lower symmetry, which will provide a more stringent test to examine the theories. We also suggest a higher-energy resolution experiment, *e.g.*, of a 10 meV resolution, to see whether or not there are fine structures and their *q*-dependence in each feature as the cluster theory predicts. Such an experiment is possible but needs a substantial improvement of the intensity for a thorough examination as performed in this work.

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