Correlation effects in the ground state charge density of Mott-insulating NiO: a comparison of \textit{ab-initio} calculations and high-energy electron diffraction measurements

S. L. Dudarev$^{1,\dagger}$, L.-M. Peng$^{2,\dagger}$, S. Y. Savrasov$^{1}$ and J.-M. Zuo$^{3}$

$^1$ Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
$^2$ Department of Electronics, Peking University, Beijing 100871, China
$^3$ Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287, USA

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Accurate high-energy electron diffraction measurements of structure factors of NiO have been carried out to investigate how strong correlations in the Ni $3d$ shell affect electron charge density in the interior area of nickel ions and whether the new \textit{ab-initio} approaches to the electronic structure of strongly correlated metal oxides are in accord with experimental observations. The generalized gradient approximation (GGA) and the local spin density approximation corrected by the Hubbard U term (LSDA+U) are found to provide the closest match to experimental measurements. The comparison of calculated and observed electron charge densities shows that correlations in the Ni $3d$ shell suppress covalent bonding between the oxygen and nickel sublattices.

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Recent years have witnessed the largely unexpected progress in the development of computational approaches to the evaluation of fundamental properties of materials from the first principles. The stimulus for this development was provided by the Hohenberg-Kohn theorem \cite{2} which establishes that the energy of the ground state of a solid is a functional of its one-electron density $\rho(r)$. The problem of accurate determination of $\rho(r)$ therefore acquires fundamental significance for the physics of materials both from the experimental and theoretical points of view. In cases where accurate experimentally measured and calculated charge densities are available (like, e.g. in the case of silicon \cite{3}), the quality of \textit{ab-initio} approximations can be assessed on the basis of the agreement between experimental and theoretical data.

The Kohn-Sham method \cite{4}, which provides a convenient way of carrying out density functional calculations, in certain cases encounters serious difficulties. For example, it predicts metallic ground states for a number of late transition metal monoxides where metal ions have partly filled electronic shells. Nickel and cobalt monoxides are often quoted \cite{5} as typical examples illustrating the failure of conventional density functional methods to describe the effective one-particle band structure of Mott insulating materials \cite{6}. Several modified density functional schemes have been proposed lately to explain the nature of large bandgaps observed for CoO and NiO. These schemes include the orbital polarization correction \cite{7}, the self-interaction correction (SIC) \cite{8} and the local spin density approximation including the Hubbard U term (LSDA+U) \cite{10,11}. The new approximations improve the description of the effective one-particle band structure of Mott insulators, and their validity is further confirmed by the recent studies of orbital ordering in transition metal compounds, see e.g. \cite{12}.

At the same time it is widely appreciated that the new ‘improved’ computational schemes represent a departure from the original formulation of density functional theory \cite{2}. The new approximations employ functionals that depend not only on the spin density of electrons $\rho_s(r)$ but also on the orbital occupation numbers that in turn depend on the choice of the basis functions. Calculations performed using the new \textit{ab-initio} schemes result in better values for bandgaps and magnetic moments \cite{11}. At the same time the use of the modified energy functionals alters the relative occupancies of $d$-states \cite{13} and alters the distribution of the charge density in the unit cell. This raises the question of how well the new functionals describe the main entity of density functional theory, namely, $\rho(r)$ itself.

In this paper we investigate this issue by comparing the calculated and experimentally observed charge density distributions. We compare the structure factors of NiO that were measured using a recently developed highly accurate electron diffraction technique \cite{14,15} and calculated theoretically using several \textit{ab-initio} linear muffin-tin orbital (LMTO)-based methods \cite{16,18}, including the LSDA+U approach.

At present, there is no sufficiently accurate experimental information on the distribution of electron charge density in the unit cell of NiO or other similar transition metal oxides. The powder X-ray diffraction techniques that were successfully used to determine the equilibrium positions of ions in a unit cell \cite{19,20}, do not have the accuracy required for observing the relatively small changes in the charge density resulting from the competition between covalent bonding and correlation effects. The convergent beam electron diffraction (CBED) technique used here takes advantage of the fact that electron beam can be focused on a small nearly perfect area of the sample and the resulting diffraction pattern can be simulated using highly accurate multiple scattering dy-
namical diffraction approach \([13]\) therefore eliminating the extinction problem that limits the accuracy of X-ray techniques. The high precision of electron diffraction measurements has made it possible to study subtle de-
ray techniques. The high precision of electron diffraction
the extinction problem that limits the accuracy of X-
ments filled oxygen 2\(p\) and empty nickel 3\(d\) states. The
bands structures of NiO calculated using either LSDA or
GGA show instead that the bandgap separates filled and
empty nickel 3\(d\) states and that NiO is therefore a Mott-
Hubbard insulator.

To characterize the distribution of electron charge den-
sity in a unit cell of NiO, we measured seven low order
energy dependent structure factors \([22]\) \(U(G)\) that are de-
defined by

\[
U(G) = \frac{2me^2}{\pi \hbar^2 G^2 \Omega} \left( \int_{\Omega} \rho^{(T)}(r) \exp(-iG \cdot r) d^3r 
- \sum_{\alpha} Z_{\alpha} \exp(-iG \cdot r_\alpha) \exp \left[ -\frac{1}{2} \left( (G \cdot u_\alpha)^2 \right) \right] \right)
\]

(1)

where \(G\) is a reciprocal lattice vector, \(m\) is the relativistic
electron mass and \(\Omega\) is the volume of the unit cell. Sum-
mation over \(\alpha\) is performed over ions in a unit cell, \(Z_{\alpha}\) is
the charge, \(r_\alpha\) is the equilibrium position and \(u_\alpha\) is
the thermal displacement of the respective nucleus. \(\rho^{(T)}(r)\) is
the electron density averaged over the thermal ensemble.

The experiment was performed using the LEO-912 \(\Omega\)
ergy-filtering electron microscope with the Gatan li-
quid nitrogen cooled sample holder. The specimen used
is a single crystal NiO cooled to about 110K. The small
rhombohedral distortion of NiO at 110 K was measured
using higher-order Laue zone lines \([26,27]\) to be \(a = 4.25\)\(\AA\) and \(\alpha = 90.044^\circ\). This small distortion was neglected in
the charge density study. The experimental CBED
patterns were recorded using a 15 eV energy-filtering
slit that was placed around the zero-loss peak. This
was done to remove the contribution from inelastically
scattered electrons that form continuous background due
to plasmon and higher energy loss processes. Off-zone-
axis systematic diffraction conditions were used to collect
diffraction intensities for reflections up to \((440)\). The
experimental patterns recorded using a slow-scan charge
coupled device (CCD) camera were processed for the sub-
sequent fitting using procedures described in \([28]\).

The refined values of the structure factors were obtained
using the EXTEL program \([15]\). Fig.2 illustrates the level
of agreement between the measured intensity variations
and multiple scattering dynamical diffraction simulations
used in the refinement procedure. The error in the mea-
sured structure factors was estimated by comparing the
results obtained using line scans taken at different posi-
tions (see Fig.2).

The calculated values of structure factors \([1]\) were
obtained by integrating the self-consistent solutions
\(\rho(r)\) of the Kohn-Sham equations found using the
LMTO method \([17]\) and various approximations for the
exchange-correlation potential. Calculations were per-
formed using three \(\kappa\)-panels and 512 k-points in the
Brillouin zone. Convergence of the calculated values
of structure factors was ensured by varying the number of
k-points and by introducing additional approximations
(e.g. by taking into account the spin-orbit coupling).

The exchange-correlation functional were taken from
\([28]\) (LSDA), \([29]\) (GGA) and \([30]\) (LSDA+U). The full
self-consistent charge density was represented by a sum
of two terms \([3]\) where the first term \(\tilde{\rho}(r)\) approximates
the density in the region between the muffin-tin spheres
and is continuous across the boundaries of the spheres.
The second term approximates the density inside the muffin-
tine spheres and is represented by a spherical harmonics
expansion \(Y_{lm}(\theta, \phi)\). Substituting this in \([1]\) we arrive at

\[
\int_{\Omega} \rho^{(T)}(r) \exp(-iG \cdot r) d^3r 
= \exp \left[ -\frac{1}{2} (G \cdot u)^2 \right] \int_{\text{int.}} \tilde{\rho}(r) \exp(-iG \cdot r) d^3r
\]

}\[
\int_{\Omega} \rho^{(T)}(r) \exp(-iG \cdot r) d^3r 
= \exp \left[ -\frac{1}{2} (G \cdot u)^2 \right] \int_{\text{int.}} \tilde{\rho}(r) \exp(-iG \cdot r) d^3r
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\[
\int_{\Omega} \rho^{(T)}(r) \exp(-iG \cdot r) d^3r 
= \exp \left[ -\frac{1}{2} (G \cdot u)^2 \right] \int_{\text{int.}} \tilde{\rho}(r) \exp(-iG \cdot r) d^3r
\]
average thermal displacements chosen set of parameters of the model, we calculated the were obtained by fitting the calculated phonon dispersion
neighbours (for the O

2

ions) and up to the second nearest (for the Ni

2+

ions). The model parameters were obtained by fitting the calculated phonon dispersion curves to the experimentally measured ones. For the chosen set of parameters of the model, we calculated the average thermal displacements (u

2

) for all the modes of lattice vibrations, and also the Debye-Waller factors for both the nickel and oxygen ions. Fig.3 shows the fitted phonon dispersion curves plotted for the (111) and (110) directions, and also the temperature dependent Debye-Waller factors. We have also investigated several other implementations of the shell model but found that they led to no significant improvement in the description of the phonon dispersion curves.

To find more accurate values of the Debye-Waller parameters for each choice of the exchange-correlation po-
tential used for ab-initio calculations we plotted two-dimensional maps of the reliability factor R treating B

Ni

and B

O

as independent variables.

The values of B

Ni

and B

O

corresponding to the minimum of the R-factor were then used to obtain the values of U(G) shown in the Table. Results listed in the Table show that the estimated values of B

Ni

and B

O

are nearly independent on the choice of approximation used in ab-initio calculations and that the spread of values of the Debye-Waller factor does not exceed 6%. The value of the Debye-Waller factor characterizing the thermal motion of electrons in the interstitial region was evaluated using two different approximations, namely, \langle B \rangle = (B_O + B_{Ni})/2 or \langle B \rangle = (M_O B_O + M_{Ni} B_{Ni})/(M_O + M_{Ni}). The difference between structure factors evaluated using these two approximations was found to be significantly smaller than the uncertainty of experimentally measured values of structure factors.

Apart from values calculated using the superposition of atomic densities, all the ab-initio methods exhibit high (better than 1%) degree of accord with experimental data, with the exception of (111) structure factor. There is a large spread among theoretical values of the (111) structure factor, which increases significantly with the inclusion of U. The structure factor of (111) is most sensitive to the changes in the distribution of the density of valence electrons, and the differences among the theoretical models shows primarily the differences in the calculated ground state valence charge density. In terms of the overall R-factor, the closest approximation to the experiment is provided by the generalized gradient approximation and by the LSDA+U approach (see Table). Better agreement with the experimental value of the (111) structure factor is achieved with the GGA.

The difference between the GGA and the LSDA+U charge density distributions is illustrated in Fig.5 where we mapped the densities calculated using the GGA and the LSDA+U approximations, subtracting from each of them the density corresponding to the non-magnetic LDA solution.
Fig. 5 shows that the symmetry of the deformation of electron density resulting from correlation effects remains the same both in LSDA+U and in GGA. At the same time there are significant differences in the radial structure of the density distributions around Ni ions calculated for the two cases. The LSDA+U approximation treats the wave functions of 3d states as ‘rigid’ objects where the Hubbard correction shifts the filled and unoccupied states in the opposite directions along the energy axis. In the GGA approximation the shape of wave functions and the population of the 3d states depends on the local density and its gradient in the interior area of nickel ions. The LSDA+U approximation relies to a larger extent on the model assumptions and on the choice of tight-binding orbitals used for treating electron correlations in a partly filled 3d shell. The GGA approximation uses the one-electron orbitals as auxiliary entities required in a calculation of total density \( \rho(\mathbf{r}) \), which is the quantity observed experimentally using high-energy electron diffraction.

Fig. 5 also shows a low resolution difference map between the experimentally observed and the GGA charge density distribution estimated using seventy six low-order experimentally measured structure factors listed in the Table (this includes transpositions and mirror reflections). The comparison between the experimental and calculated distributions confirms the trends revealed by the GGA and LSDA+U analysis showing that correlation effects are responsible for the suppression of covalent bonding between the metal and oxygen sublattices (this effect manifests itself in the reduction of the charge density in the areas between the oxygen and nickel ions). This agrees with the analysis of a similar effect discovered in [24] for uranium dioxide. The charge density in a unit cell of real NiO is more concentrated around atomic nuclei and it also shows tendency towards increasing in the region between ions of the same type. Qualitatively this may be interpreted as an indication that Ni d-orbitals in fact have the shape that is different from that predicted by either the GGA or the LSDA+U calculations.

There are several reasons responsible for the observed inaccuracy of \textit{ab-initio} approaches. For example, the LSDA+U approximation is based on the mean-field treatment of correlation effects [24]. There could be other, more fundamental, circumstances leading to the difference between the calculated and experimentally observed charge density distributions. One of the ideas behind the development of more accurate approaches to the treatment of electron correlations in transition metal compounds consists in that the new approaches are intended to be used for evaluating the parameters entering tight-binding \textit{many-body} models of electron-electron interactions. These models are always based on a particular choice of orbitals associated with each of the ions in the solid. Our results show that the accuracy of the assumption that the charge density may be decomposed into contributions associated with individual ions, is limited, and this conclusion agrees with the analysis performed in Ref. [3]. To describe correlation effects in oxides where covalency as well as correlation effects play a significant part, it may be necessary to take into account changes in both the shape and occupation of localized electronic orbitals. A second-quantized many-body model describing intersite hopping and on-site Coulomb interaction between electrons may prove to be sufficient for accounting for the positions of the main peaks in the spectrum of excited states of an oxide. At the same time even the exact solution of the model may not be capable of giving a sufficiently accurate description to the the ground-state properties of the system such as the distribution of the charge density of electrons in a unit cell. The approach developed in this paper can also now be applied to test the accuracy and to compare several other \textit{ab-initio} methods that we did not consider above, for example, the self-interaction correction [1] or the first-principles Hartree-Fock approximation [36].

In summary, by combining a recently developed high accuracy electron diffraction technique with \textit{ab-initio} calculations, we investigated how electron correlations in the Ni 3d shell influence the distribution of charge density in the unit cell of NiO. By comparing the experimentally measured values of structure factors with values calculated using several different \textit{ab-initio} approaches we found that the structure factors evaluated using the generalized gradient approximation and the LSDA+U approach agree best with the available experimental information. The experimental data show that the degree of covalent bonding in NiO is smaller than that predicted by theoretical calculations.

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\(^1\)Permanent address: Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
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**FIGURE CAPTIONS**

FIG. 1. The total density of states plots of NiO calculated assuming (a) a non-magnetic ground state and the local density approximation (b) the type II AF ground state and the local spin density approximation (c) the type II AF ground state and the generalized gradient approximation (d) the type II AF ground state and the local spin density approximation corrected by the Hubbard U term (LSDA+U). $\epsilon_F$ denotes the Fermi energy and $\epsilon_{F+U}^{exp}$ shows the experimentally observed position of the bottom of the conduction band.

FIG. 2. An example of NiO structural factor measurement using convergent beam electron diffraction (CBED). The top is the experimentally recorded diffraction pattern with (220) and (440) strongly diffracted. The structural factors of (220) and (440) were obtained by fitting intensities along the indicated lines. The best fit is shown in bottom right. The schematic diagram on bottom-left shows the formation of CBED by focusing the electron beam on the top of crystalline specimen.
FIG. 3. Plots illustrating the fitting of the phonon dispersion curves along \((111)\) and \((110)\) directions, and the comparison between the values of the Debye-Waller factors evaluated using the shell model and found by comparing the experimentally measured and calculated structure factors.

FIG. 4. A map showing the dependence of the R-factor on the two Debye-Waller factors \(B_{Ni}\) and \(B_{O}\) characterizing the amplitude of thermal vibrations of Ni and O ions in NiO. Values \(B_{Ni} = 0.133 \ \text{Å}^2\) and \(B_{Ni} = 0.244 \ \text{Å}^2\) correspond to the minimum of \(R = 0.0049\).

FIG. 5. Cross-sections of charge density distribution in the \((100)\) plane of NiO calculated using the GGA and LSDA+U approximations. The two contour maps on the left-hand side show the difference between the self-consistent density distributions and the density calculated using the local density approximation for a non-magnetic ground state. The map on the right-hand side shows the difference between the experimentally observed charge density distribution and the distribution calculated using the generalized gradient approximation.
The observed and calculated values of structure factors for NiO. The Debye-Waller temperature factors $B_{Ni} = 8\pi^2\langle u_{Ni}^2 \rangle$ and $B_O = 8\pi^2\langle u_{O}^2 \rangle$ for each calculated set were introduced following the procedure described in the text. The energy of the incident electrons equals $E_0 = 119.5$ keV. All the values listed in the table are given with the opposite sign and in Å² units (see Ref. [3]). The $R$-factor is defined as $R = \sum_G W_G|U^\text{th}(G) - U^\text{exp}(G)|/|U^\text{exp}(G)|$, where $U^\text{th}(G)$ are the calculated and $U^\text{exp}(G)$ are the experimentally measured values. The weight factors $W_G$ are given by $W_G = \sigma_G^{-1}/(\sum_G \sigma_G^{-1})$ where $\sigma_G$ represent experimental uncertainties. The error-bar of the $R$-factor, $\delta R$, is given by $(\delta R)^2 = \sum_G W_G\sigma_G^2/|U^\text{exp}(G)|^2$. Abbreviations NM and AF refer to non-magnetic and antiferromagnetic states, respectively.

| h  | k  | l  | observed values (std. dev. $\sigma_G$) | ATOMS | LSDA (NM) | LSDA (AF) | LSDA + U (AF) | GGA (AF) | GGA + U (AF) |
|----|----|----|----------------------------------------|-------|-----------|------------|--------------|----------|-------------|
| -U | (111) | 0.135 | 0.0235 | 0.0237 | 0.0235 | 0.0239 | 0.0247 | 0.0244 | 0.0251 |
| -U | (111) | 4.632·10⁻² | (±0.012·10⁻²) | 4.401·10⁻² | 4.555·10⁻² | 4.597·10⁻² | 4.668·10⁻² | 4.642·10⁻² | 4.708·10⁻² |
| -U | (220) | 9.083·10⁻² | (±0.022·10⁻²) | 9.486·10⁻² | 9.187·10⁻² | 9.204·10⁻² | 9.181·10⁻² | 9.173·10⁻² | 9.151·10⁻² |
| -U | (311) | 6.640·10⁻² | (±0.036·10⁻²) | 6.756·10⁻² | 6.709·10⁻² | 6.716·10⁻² | 6.705·10⁻² | 6.703·10⁻² | 6.694·10⁻² |
| -U | (222) | 5.220·10⁻² | (±0.036·10⁻²) | 5.098·10⁻² | 5.098·10⁻² | 5.116·10⁻² | 5.103·10⁻² | 5.103·10⁻² | 5.103·10⁻² |
| -U | (400) | 4.456·10⁻² | (±0.018·10⁻²) | 4.436·10⁻² | 4.455·10⁻² | 4.456·10⁻² | 4.456·10⁻² | 4.456·10⁻² | 4.456·10⁻² |
| -U | (440) | 4.214·10⁻² | (±0.034·10⁻²) | 4.214·10⁻² | 4.214·10⁻² | 4.214·10⁻² | 4.214·10⁻² | 4.214·10⁻² | 4.214·10⁻² |

* values calculated using the shell model (see text)
** R-factor evaluated on the basis of experimental uncertainties $\sigma_G$
Debye-Waller factors (Angstrom²) versus Temperature (K)

Frequency (THz) versus q = 2πζ/a

- GGA – Ni
- GGA – O
- Shell model – Ni
- Shell model – O

Experimental

Shell model

Modes:
- LO
- TO
- T₁O
- TA
- LA
- T₂A
