Chapter 2

NiO

As stated before, the first-row transition-metal oxides are among the most interesting series of materials, exhibiting wide variations in physical properties related to electronic structure. The optical and magnetic behavior, in particular, forms the basis for the enormous range of applications. As a result, they have been the subject of extensive experimental and theoretical investigations for the past several years. In this chapter we will address some features (for a review) which form an essential background in studying these materials. Such as NiO, one of the most favored antiferromagnets, is a prototypic system for strong electronic correlations with high spin AF$_2$ structure at low temperatures and has a simple crystallographic rocksalt structure with a lattice constant of 0.417 nm (see Fig. 2.1). There are two components of spin configurations due to the non-local exchange interaction. For the first component, the direct exchange interaction between the nearest neighbour of Ni ions favors paring of spins to lower energy. For another one, a very strong interaction comes from the superexchange between the next-nearest neighbour of Ni ions [35, 36]. This makes the antiferromagnetic spin structure for the ground state of NiO.

2.1 Experimental and theoretical studies

In the field of solid state physics, many experimental and theoretical attempts have been made to investigate the interesting physical properties of the 3$d$ transition-metal oxides, which are characterized by the partially occupied 3$d$–orbitals. This range of properties also imposes many difficult problems of scientific understanding. Especially, the insulating behavior of these materials has been extensively studied for several decades.

Mott and Hubbard have reported that the strong $d$–$d$ Coulomb interaction is essential to explain why some of transition metal compounds play a major role as insulators with partially filled 3$d$ bands, while the others exist as metals [3, 37]. The transport of electrical charge in the solid state is provided by electrons that are subjected to the Coulomb interaction with the ions and the other electrons. The importance of a large Coulomb interaction $U_{dd}$ is implicit in the common Anderson superexchange theory [38], and is fundamental to concept of the Mott-Hubbard insulator. When the $d$–$d$ Coulomb interaction is larger than the band width, 3$d$–orbitals are localized and the magnitude of the band gap is determined by the $d$–$d$ Coulomb
Later, experimentally the powerful characterizations such as the combination of x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) measurements of cleaved single crystals of NiO have provided unambiguous evidence that the intrinsic charge transfer gap is 4.3 eV \[39\]. In addition, the band gap of \(\sim 4\) eV (\(p \rightarrow d\) character) has been indicated by a range of spectroscopic techniques including optical absorption \[40\], x-ray absorption spectroscopy (XAS) at the oxygen K-edge \[41\], and electron energy loss spectroscopy (EELS) \[42\]. Computationally it has been shown that the band gap of NiO is not determined by \(d\)–\(d\) Coulomb interaction, but by ligand-to-\(d\) charge transfer energy (\(\Delta\)) by analyzing the photoemission spectrum with the configuration interaction cluster model approach \[43, 44\]. By using this calculation, one predicts the gap of 5 eV whereas the density functional theory predicts a gap of 0.3 eV \[10\]. Based on the local-cluster and single-impurity approach, a classification scheme have been proposed \[11\], where the TMOs can be classified into two regimes according to the relative magnitude of \(\Delta\) and \(U_{dd}\). For the Mott-Hubbard regime, \(\Delta > U_{dd}\), the band gap is determined by \(d\)–\(d\) transition and its magnitude is given by \(U_{dd}\). For the charge transfer regime, \(\Delta < U_{dd}\), the magnitude of a \(p \rightarrow d\) band gap is \(\Delta\).

Alternatively, several theoretical studies have been carried out, to understand the electronic structure and band gap of NiO. The band structure calculations of TMOs were treated by the local-spin-density approximation (LSDA) as described in Ref. \[10\]. This model have been successfully applied to describe many details of electronic structure, magnetic coupling, and character of the band gap since a long time. However, the local density approximation (LDA), which is widely used in solid-state physics, fails to describe the band structure of NiO as an insulator and predicts it to be as a metal \[45\]. This deficiency of the LDA is not fully solved by the generalized gradient approximation (GGA) level of theory, which still provides too small band gap of NiO, indicating either a metal or a semiconducting character \[46, 47\]. It has been suggested that the problem of the LDA (and the GGA) for properly describing a narrow band gap is related to the insufficient cancellation of the self-interaction correction (SIC) inherent in the local exchange function. The SIC-LDA introduces a better description of band gap (\(\sim 3\)
2.2 NiO and its low-lying excited states

Magnetic and optical properties of TMOs are governed by the ground state and low-energy excitation spectrum of the $d$ shell of the central TM ion. These spectra are successfully fit to the crystal field theory [53]. Thus, it is the strong Coulomb interaction between the $3d$ electrons that leads to an energy splitting of the $d^n$ and $d^{n+1}$ states. The low-lying excited states, so-called dipole-forbidden $d$–$d$ transitions, appear as weak features in optical spectra. All $d$–$d$ transitions violate the parity selection rule $\Delta l = \pm 1$ (the Laporte forbidden character in centrosymmetric cases). For the earlier work, Newman and Chrenko measured the $d$–$d$ transitions in bulk NiO by using absorption spectroscopy [54]. Only recently, the experimental data have become available for $d$–$d$ transitions of the bulk and (001) surface of NiO [55, 56, 57, 58, 59, 60]. These results have been revealed in a range $0.5 \rightarrow 3.0$ eV by means of electron energy-loss spectroscopy (EELS). The great advantage of exciting such transitions with slow electrons is the possibility of excitation by electron exchange, additionally. The multiplicity-conserving ($\Delta S = 0$), as well as multiplicity-changing transitions ($\Delta S = \pm 1$), are easily observable with EELS if a suitable energy of the incident electrons is chosen [2]. It has been supposed that the intensity of triplet-singlet $d$–$d$ transitions in NiO depends on the antiferromagnetic ordering of the magnetic moments [61, 62, 63], yet an investigation of $d$–$d$ transitions above the Néel temperature has not been reported.

The calculated $d$–$d$ excitation energies of the bulk and (001) surface of NiO were investigated at first-principles unrestricted Hartree-Fock level of theory by Mackrodt and Noguera [64]. These results allow for comparisons with optical absorption and EELS and with the theoretical works based on first-principles multi-reference CEPA [55] and CASCF/CASPT2 [65, 66] calculations of embedded clusters of the type (NiO$_6$)$^{10-}$ and (NiO$_5$)$^{8-}$. From the results of these calculations, which have included electron correlation in different ways and at different levels of sophistication, it has been concluded [55, 65, 66] that the inclusion of electron correlation effects is an essential prerequisite for an accurate description of $d$–$d$ excitations in NiO. These results suggest that for NiO with its highly localized $d$–$e$-electrons resulting from strong on-site Coulomb and exchange interaction, the contribution from electron correlation
is approximately 0.2 – 0.3 eV for the entire of one- and two-electron excitation.

2.3 Second Harmonic Generation

The second order nonlinear optical technique, second harmonic generation (SHG), deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic fields, related in frequency, phase, or other physical properties. The reflected SHG intensity from media, which lack a center of inversion symmetry, is generated by the harmonic polarization in a layer about one quarter optical wavelength thick in a transparent dielectric, or in the absorption depth in the case of a strongly absorbing medium. These early observations are therefore not surface specific. SHG with a center of inversion symmetry was first observed by Terhune et al. [67] in calcite. They proposed a nonlinear term of quadrupolar origin in the form of a second harmonic polarization proportional to the fundamental field and its gradient. Pershan [68] showed that in media with inversion symmetry the second harmonic polarization source term may be written in the general form, \( P_i(2\omega) = \chi_{ijk}^Q E_j(\omega) E_k(\omega) \), where \( Q \) denotes a quadrupolar transition taken into account.

This source term in a non-absorbing dielectric is ninety degrees out of phase with the nonlinear SH polarization induced in the presence of an applied dc electric field. At such an interface a discontinuity in the normal component of electric field and in the tensor components of the quadrupolar susceptibility occur.

The developments of SHG at interfaces with inversion symmetry during the sixties are summarized in a fairly comprehensive paper by Bloembergen et al. [69]. Shen [70] has also reviewed the progress made during the eighties. Refined theoretical analysis carefully examined the discontinuities in the normal component of the electric field, \( E \), as one passes from a centrosymmetric medium with dielectric constant \( \varepsilon_1 \) through a dipolar sheet with dielectric constant \( \varepsilon' \) to a centrosymmetric medium with dielectric constant \( \varepsilon_2 \). This review paper defines an effective surface nonlinear susceptibility tensor \( \chi_{ijk}^S \) which clearly delineates the three effects as:

- The electric dipole term arises from the lack of inversion symmetry at the interface. This term may be significantly enhanced by absorbed monolayers of polar molecules.
- The non-local electric quadrupolar contribution to the surface nonlinearity is controlled by the strong gradient in the normal component of the electric field. This contribution is diminished when the difference in dielectric constants or indices of refraction between the two media at the interface is small.
- The third term results from the discontinuity in the volume quadrupole moment densities of two bulk media defining the interface. The gradient operator in this case acts on \( \chi_{ijk}^Q \). This term, when integrated across the interface, yields the difference of two volume susceptibilities. It represents a bulk contribution which cannot be separated from the other two specific surface contributions for one single interface.

The effective nonlinear surface tensor \( \chi_{ijk}^S(2\omega) \) must reflect the symmetry characteristic of the surface. Here the index \( i \) refers to the components of the second harmonic field, and
2.3. Second Harmonic Generation

Let $j$ and $k$ be the Cartesian components of the fundamental field. For the surface of an isotropic medium, normal to the $z$-direction, three independent elements exist with the following index combinations: $(xxz) = (xzx) = (yyz) = (yyz)$, $(xxx) = (xyz)$, and $(zzz)$.

For centrosymmetric antiferromagnetic NiO, SHG spectra due to the combined contributions from magnetic-dipole (MD) and electric-dipole (ED) transitions between the $3d^8$ levels of Ni$^{2+}$ ion were observed by Fiebig and coworkers [17]. In this experiment, the intensity of the SH signal with distinct spectral features, which is observed in the investigated $1.6 - 2.3$ eV energy range of $2\hbar\omega$, is comparable to the intensity measured in noncentrosymmetric compounds such as antiferromagnetic Cr$_2$O$_3$ or YMnO$_3$ in which the SH process is of the ED-type [71, 72]. They have shown that an increase of SH intensity from the forbidden ED transitions occurs due to their resonance enhancement of both the incoming and the outgoing beams (processes of MD absorption at the frequency $\omega$ and ED emission at $2\omega$ are resonant). A quadratic coupling of nonlinear polarization to the order parameter was also found. Fiebig et al. [17] reported that the $\Gamma_3^+$, $\Gamma_4^+$, $\Gamma_5^+$, and $\Gamma_2^+$ states, into which the $3\Gamma_5^+$ state was split by the spin-orbit interaction, were clearly identified both in the absorption spectra and in the low-temperature SH spectra (in the region of lowest $3d^8$ electronic transitions with incident and emitted [001]-polarized light). Then, they presented the energy diagram of the corresponding $3d^8$ levels of the Ni$^{2+}$ ion (which were split by the octahedral crystal field, the spin-orbit interaction, and the exchange field below the Néel temperature). The energy scheme derived from this experiment serves as a good reference point to our results as documented in section 4.4.2.

From the previous examples, one can conclude that SH generation is a versatile tool that might have numerous technological and experimental applications. In particular, applying it to NiO, it can be used for characterization of its magnetic structure. It is known that for this antiferromagnetic material with a Néel temperature of 523 K, several magnetic-moment ordering types are possible. However, the observation in this material from the linear optical experiments is more complicated than in ferromagnetic one since the reduction of the spatial symmetry is not linked to an imbalance in the occupation of majority- and minority-spin states. In recent years, Dähn et al. [18] have shown the symmetry arguments how optical SHG can be used to detect antiferromagnetic spin arrangements at surfaces and in thin films and also to separate antiferromagnetic phases from the paramagnetic and ferromagnetic ones. This is a remarkable fact since paramagnetic structure exhibits an inversion symmetry as the antiferromagnetic state. However, the two states usually differ in the allowed space transformations, and this fact can be used to detect different phases by using different polarizations of incoming light. The full classification of all possible SH responses from the domains of antiferromagnets is presented in Ref. [73]. Theoretically, the SHG response was described in the paper of Hübner and Bennemann [34]. The expression for the nonlinear optical susceptibility tensor, $\chi$, was obtained from the corresponding electronic structure of material.

1 Recently, a spatially resolved polarization dependent x-ray absorption spectroscopy was used in order to fully characterize the AF structure at the surface of NiO. All 12 possible domain types originating from the bulk termination were distinguished. The measurements also showed an evidence that the magnetic moments have the same orientation as in the bulk NiO which is in contrast to sputtered surfaces, where magnetic moments lie within surface plane, forming a magnetically relaxed structure.