Chapter 1

Introduction

1.1 Oxides and Their Interfaces

From the very advent of human civilization people were dealing with metal oxides. They were admiring the beautiful green color of old copper roofs, fighting against rust on their kettles and swords, attributing magic powers to noble metals since they never oxidize. Ancient Chinese were using magnetite to orientate their boats on high seas, while medieval Europeans were using various metal oxides to illuminate[1] their books. During the past decades of investigation, the research mainly focused on the structural and electronic properties of bulk oxides. The problems of strong electronic correlations have attracted theoreticians towards magnetic oxides already in the 1960's. This investigation resulted in creating theoretical models which describe the ground state of these materials properly (e.g. the Hubbard model [1]). They have been successfully applied also to another important class of oxides, high-T_c superconductors. However, with the advent of high-fluence lasers, which made nonlinear (magneto-)optics possible [2], the description of non-equilibrium states became neccessary. On the other hand, the scientific understanding of oxide *surfaces and interfaces* is still in its infancy, although in the last years many scientific programs have been launched in order to clarify the physics of oxide interfaces.

From the beginning of computer technology, long-term (magnetic) data storage and temporary (semiconductor-based) data storage have existed and have been developed separately. Semiconductor industry has been able to fit more and more transistors onto a silicon chip while magnetic-recording industry has been shrinking the size of the reading head, increasing the storage density. Nowadays, the demands of the market seemingly push these two areas together: there is a need for nonvolatile memory chips where the information remains stored even after switching the computer off, and on the other hand the need for the speed of the storage devices may eventually eliminate the designs which rely on the mechanical motion of the elements (like currently used hard disk drives) [3]. The field which marries the two hitherto separate areas is magnetoelectronics, and the devices which are supposed to supersede the conventional random access memories and hard disks are Magnetic Random Access Memories (MRAMs).

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[1] Illumination is a medieval book illustration in various shades of red.

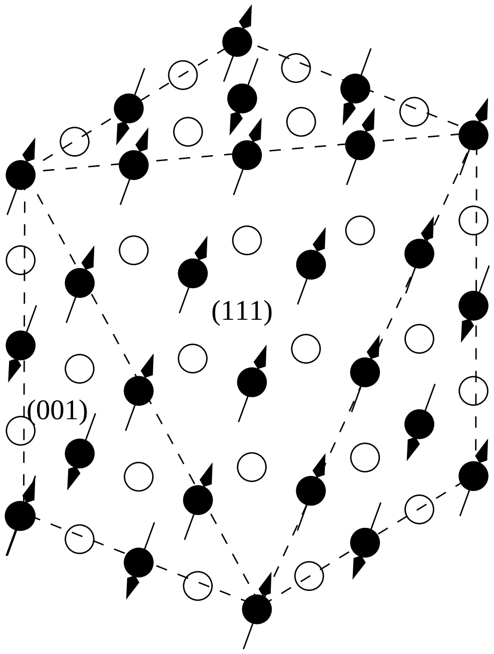

Figure 1: Surfaces of the cubic antiferromagnet NiO.

One of the most important components of the designed MRAMs are tunneling magnetoresistance (TMR) devices, where the read-out current passing through the device depends on the relative magnetization of two ferromagnetic layers. The central layer of this trilayer structure consists of an oxide sandwiched between a soft and a hard magnetic layer[2]. For these technological applications it is necessary to develop a technique to study buried oxide interfaces. Already the preparation of transition-metal oxides is a challenge and requires a method to characterize the structure and magnetism of these materials. Such a technique can be optical second harmonic generation (SHG), which is easy to implement, sensitive to antiferromagnetism and addresses surfaces and interfaces of materials which possess central symmetry. One of the most favored antiferromagnets is nickel oxide (NiO), which is a prototypic system for strong electronic correlations and has a simple crystallographic rock-salt structure (see Fig. 1). However, this material is not easily accesible for the experimental study, since it cannot be grown on nickel due to a large lattice mismatch (20%). To the best of our knowledge, the understanding of its detailed spin structure is scarce - even the spin orientation on the ferromagnetically ordered and antiferromagnetically coupled (111) planes[3] are not known. The technique presented in this work can shed some light on that issue, and answer some other important questions related to antiferromagnetic oxide interfaces.

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[2] These two layers are often composed from the same material but of different thicknesses.

[3] Neither the detailed interatomic distances.

1.2 Second Harmonic Generation

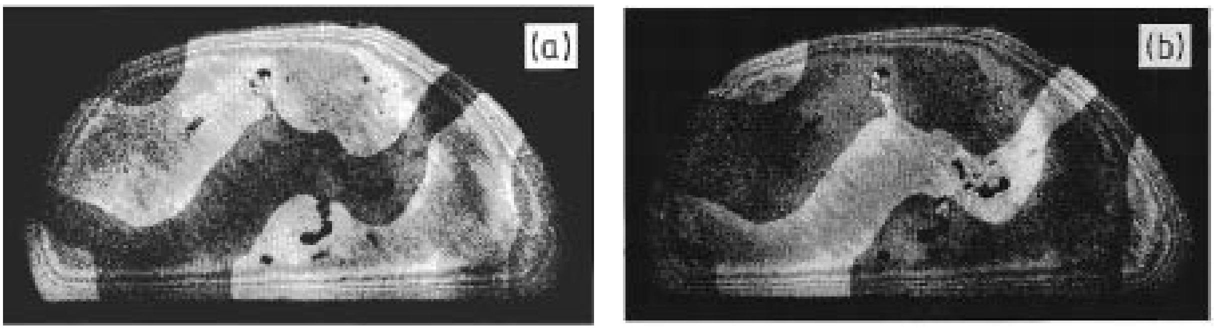

Figure 2: Bulk AF domain imaging by Fiebig *et al.* [4]. Images taken with right (a) and left (b) circularly polarized light.

As stated before, SHG has the unique potential to become a tool for investigating buried oxide interfaces, where other techniques fail. Until now, it has been proven to be a very useful technique for the investigation of ferromagnetism at surfaces. The obvious question is if this technique can also yield some new information in the case of more general spin configurations, such as antiferromagnetic (AF) ordering at interfaces. An experimental answer to this question has been provided by Fiebig *et al.* [4, 5], who obtained a pronounced optical contrast from AF 180° domains of *rhombohedral* bulk Cr_2O_3. This experiment, which is of great significance for us, will be described later in detail (page 9). Since it is known that, in *cubic* materials, within the electric dipole approximation, optical SHG originates only from surfaces, interfaces, or thin films, an important question is if SHG is also sensitive to antiferromagnetism at surfaces of cubic antiferromagnets.

Experimental techniques for the detection of AF domain *walls* using linear optics in some special geometries were elaborated already in the 1950's [6]. The *interior* of the domains has been visualized in piezoelectric AF crystals using a linear magneto-optical effect [7]. However, linear optical experiments suffer from mixing the desired signal with a contribution from other linear effects, such as birefringence or dichroism. A review of linear optical experimental methods for the investigation of AF domains is given by Dillon [8]. Only neutron diffraction [9] and x-ray crystallography[4] techniques and SHG are able to address the balanced spin structures. All other techniques are not conclusive, for instance the linear dichroism [10] couples to the order parameter squared and consequently cannot distinguish antiferromagnetism from ferromagnetism.

The observation of the domain structure in antiferromagnets is more complicated than in ferromagnetic materials since the reduction of the spatial symmetry in the antiferromagnetic phase is, unlike for ferromagnets, not linked to an imbalance in the occupation of majority and minority spin states.

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[4] X-ray crystallography addresses the structural properties of the sample. In antiferromagnets, it detects the unit-cell doubling rather than antiferromagnetism, and thus it fails in materials like Cr_2O_3.

Nonlinear optics exhibits an additional degree of freedom, since its elementary process involves three photons instead of two in linear optics. For that reason, some authors, e.g. Fröhlich [11] suggested the application of nonlinear optics even for k-selective spectroscopy, since multi-photon phenomena allow for the "scanning" of a small part of the Brillouin zone, at least for semiconductors. Recently, non-linear optics has attracted more and more attention to the investigation of magnetism due to its enhanced sensitivity to twodimensional *ferromagnetism* [12, 13]. The magnetic effects are usually much stronger than in linear optics (rotations up to 90°, pronounced spin-polarized quantum well state oscillations [14, 15], magnetic contrasts close to 100%) [16, 17]. An example of ferromagnetic effects measurable *only* by SHG deals with the existence of surface magnetism in very thin films of Fe/Cu(001) and is given in Ref. [18]. Nonlinear optical effects were invoked to investigate high temperature superconductors [19, 20] and to study structures composed from alternately ferro- and antiferromagnetically ordered thin films [21][5]. SHG in strong magnetic fields has been predicted also in vacuum [22], although the size of the effect is questionable [23]. However, the first experiments concerning the detection of the AF domains in materials such as Cr_2O_3 were carried out only recently [4, 24]. Already in the 1970s, it has been proposed [25] that experimental studies of dc magnetic and electric field-induced SHG could become an effective method of determining the crystal structure of solids, the symmetry of which cannot be investigated by other methods. Extending this idea towards surface crystallography provides us with a new technique for determining the spin configuration in a given surface structure. In turn, it permits to use a known magnetic configuration as a reference system for the determination of the surface structure. All the mentioned information is more difficult or even impossible to obtain in linear optics, and moreover other linear methods like neutron scattering, albeit capable to see AF domains, have difficulties to probe AF spin configurations. In addition, the neutron diffraction suffers from large acquisition times and is therefore not suitable for dynamics.

1.3 The Scope of this Work

The arguments mentioned hitherto suggest that the technique of optical second harmonic generation (SHG) will play a key role in the investigation of complicated magnetic sandwich structures. Therefore, our work aims at the theoretical investigation of SHG from antiferromagnetic surfaces and interfaces. The project can be characterized by the following points:

- Symmetry classification. We classify the symmetries of antiferromagnetic surfaces and determine the influence of the symmetries on the nonlinear magneto-optical susceptibility tensor. Using these results we check the possibility of domain imaging. Until now, the group-theoretical classification was devoted to revealing the existing tensor elements for a given symmetry for bulk systems, and without relation to SHG. In the experiment, however, SHG results from the specific tensor elements,

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[5] The antiferromagnetic Cr is assumed there to give no contribution to magnetization-induced SHG.

and one often is interested in the particular spin structure rather than the name of the appropriate symmetry group. Our work aims at filling this missing link.

- Domain imaging. Closely related to the previous, our work investigates the possibility of domain imaging on antiferromagnetic surfaces. Until now, it has been proven that linear optics cannot yield trustworthy results, and the only other method, neutron scattering, is at least cumbersome in application. Also, the AF bulk domains have been experimentally observed by nonlinear optics. Our work will investigate the conditions under which also the AF surface domains can be imaged in SHG.

- Spin Reversal. Until now, the notions of time-reversal and spin-reversal were used indiscriminately in the symmetry analysis. However, in nonlinear optics the applicability of time-reversal is not obvious, on the other hand the spin degree of freedom must show up in the symmetry analysis by space operations. In this work, we propose a consistent description of the dynamic process of SHG and define the notions of reciprocity, time-reversal and moment-reversal for the use in the symmetry analysis of nonlinear optics.

- Electronic theory. Based upon the previous points, we will propose a theoretical framework which will allow for the calculation of the nonlinear magneto-optical spectra from antiferromagnetic interfaces. Our theory, aiming at the most general level of description (ability to treat para-, ferro-, and antiferromagnetism on equal footing) will *not* be an *ab initio* theory. Also, ground state features (such as structure optimization) will not be addressed in our approach. However, it successfully identifies the spectral lines favorable for nonlinear optics, and magneto-optics in particular. The theory forms a basis for the description of nearly all elements: only the systems with electronic configuration d^5 and those with f-electrons cannot yet be treated within this framework. The extension of our theory towards d^5 systems is straightforward. The calculations are performed for the NiO (001) surface, but an extension to other AF oxide surfaces is possible.

- Femtosecond dynamics. Based on the electronic calculations, we present the results of our simulations of an SHG pump-and-probe experiment. These results concern both spin- and charge-dynamics (dynamics of the antiferromagnetic and paramagnetic tensor elements) and reveal interesting dynamical properties of the antiferromagnetic response within the femtosecond regime.