

Optical Spectroscopy of Quantum Spin Systems

Reproduced on the front cover is the first direct observation of a pair of strongly-coupled giant quantum spins, embedded in a quasi one-dimensional tulip system. This incredible snap-shot was taken by Markus Grüninger in the countryside of Leiden, The Netherlands, in March 1996.

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Rijksuniversiteit Groningen

Optical Spectroscopy of Quantum Spin Systems

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ter verkrijging van het doctoraat in de
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door

Andrea Damascelli

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te Milaan (Italië)

Promotor: Prof. dr. D. van der Marel

*Saranno le stelle più luminose
a guidare il tuo cammino.
A te, il trovarle.*

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Chapter 1

Introduction

1.1 Strongly Correlated Electron Systems

One of the most challenging branches of solid state physics, from the intellectual point of view, is represented by the investigation of *strongly correlated electron systems*, i.e., compounds whose properties are dominated by strong electron-electron correlations. This is the case when the on-site electron-electron repulsion U is much larger than the energies associated with the overlap of atomic orbitals belonging to different atoms. Because these energies are characterized, in a solid, by the width W of the energy band under consideration, a large U/W ratio is expected in systems involving well-localized electrons like the $4f$ and $5f$ electrons of the rare earths and the actinides, respectively, but also the d electrons of the transition metals (TM) [1].

The importance of electron-electron correlations in influencing the basic properties of a compound can be understood considering the case of CoO which, although not discussed further on in this thesis, represents a very typical example. This oxide, if treated within the independent-electron approximation (i.e., writing the total wavefunction of the N -electron system in the form of an antisymmetrized product of single-electron wavefunctions), is expected to be metallic, with an odd number of electrons per unit cell and a partially filled d band. In reality, as a consequence of strong correlations, which are suppressing charge fluctuations and therefore the electrical conductivity, CoO is a rather good insulator at all temperatures, with an optical gap of about 6 eV [1,2].

More in general, strong electron-electron correlations can give rise to a large variety of peculiar phenomena, the most famous being probably high-temperature superconductivity, heavy-fermion and Kondo-insulating behavior, spin-Peierls phase transition, spin-gap phenomena, and colossal magnetoresistance. For the description of these collective phenomena, and for the development of appropriate microscopic models, it is useful to investigate the elementary excitations of these materials. In fact, the excitations from the ground state to the lowest excited states reflect the interplay between quantum magnetism and low energy charge degrees of freedom, a fingerprint of strong electron-electron correlations.

1.2 Optical Conductivity

A powerful tool to study the elementary excitations of an N -particle system is optical spectroscopy. This technique consists of shining light of different frequencies onto the sample under investigation, and of observing which frequencies are absorbed by the material itself. In the course of this thesis we will present transmission and reflectivity data obtained in the frequency range extending from the far infrared to the ultra violet (i.e., from 4 meV to 4 eV). Additional information was obtained by performing the optical experiments with linearly polarized light, in order to probe the possible anisotropy of the crystals, and varying the temperature of the samples between 4 and 300 K. The optical conductivity was then obtained by Kramers-Kronig transformations [3], in the regions where only reflectivity spectra were measurable, and by direct inversion of the Fresnel equations [4], wherever both reflection and transmission data were available.

For the analysis of the conductivity spectra presented in the course of the thesis, it is useful to derive a functional expression for the optical conductivity of a system of N electrons, in the presence of an externally applied time-dependent electric field. From the fluctuation-dissipation theorem, which relates the fluctuations of a system described by a correlation function to the dissipations described by the imaginary part of a susceptibility, it follows that the dynamical conductivity is related to the equilibrium current-current correlation function $\chi(\omega)$ [5–7]:

$$\sigma(\omega) = \frac{1}{i\omega} \left[\chi(\omega) - \frac{nq_e^2}{m} \right], \quad (1.1)$$

where n is the density of electrons, and q_e and m are the electronic charge and mass, respectively. The retarded correlation function $\chi(\omega)$ is defined as:

$$\chi(\omega) = \frac{i}{V} \int_0^\infty dt e^{i\omega t} \langle [\hat{\mathbf{j}}(t), \hat{\mathbf{j}}(0)] \rangle, \quad (1.2)$$

where V is the volume of the system, and $\hat{\mathbf{j}} = \partial \hat{\mathbf{P}} / \partial t = i[\hat{H}, \hat{\mathbf{P}}]$ is the current operator (being $\hat{\mathbf{P}}$ the polarization operator and \hat{H} the Hamiltonian describing the system in presence of the external electric field). If we denote by $|n\rangle$ and E_n the eigenstates and eigenvalues, respectively, of the many-body Hamiltonian of the system, the current-current correlation function can be written as:

$$\chi(\omega) = \frac{1}{V} \sum_{n \neq g} |\langle n | \hat{\mathbf{j}} | g \rangle|^2 \left(\frac{1}{\omega + E_n - E_g - i\eta} - \frac{1}{\omega - E_n + E_g + i\eta} \right), \quad (1.3)$$

where g refers to the ground state of the N -electron system. From eq. 1.1 and 1.3, the real part of the optical conductivity, $\sigma_1(\omega)$, becomes:

$$\sigma_1(\omega) = \frac{\pi}{V} \sum_{n \neq g} |\langle n | \hat{\mathbf{j}} | g \rangle|^2 \frac{\delta(\omega - E_n + E_g)}{E_n - E_g}, \quad (1.4)$$

which defines the excitation spectrum of the system. It consists of a series of sharp lines (corresponding to the excitation between the ground state $|g\rangle$ and the excited states $|n\rangle$), which will merge into a continuum upon increasing the number of electrons, making $\sigma_1(\omega)$ a continuous function of frequency.

For the quantitative analysis of the conductivity spectra obtained in the experiments, we will in particular make use of the integral, with respect to the frequency, of the real part of the dynamical conductivity $\sigma_1(\omega)$, which is give by:

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi q_e^2}{\hbar^2 V} \sum_{n \neq g} (E_n - E_g) |\langle n | \hat{\mathbf{x}} | g \rangle|^2, \quad (1.5)$$

where $\hat{\mathbf{x}} = \sum_i \hat{\mathbf{x}}_i$ is the sum of the position operators of the electrons.

1.3 Scope of this Thesis

In the course of this thesis we will present optical data obtained on a number of different compounds, whose common feature is that they all belong to the class of strongly correlated electron systems. We will discuss in detail the detected lattice vibrational modes and the electronic and/or magnetic excitation spectra, in order to learn about the crystal structure of the different systems, and their electronic and magnetic properties like, e.g., ground state configuration, electron-phonon coupling, and spin-charge interplay.

In chapter 2 we will present the optical spectra of several transition-metal (TM) mono-silicides (FeSi, CoSi, and MnSi), with particular emphasis on FeSi, which shows Kondo-insulating behavior at low temperature [8]: Total compensation of the local magnetic moment on the Fe sites together with the opening of a narrow electronic gap. Based on the discussion of our infrared spectra (in particular, of the coupling between vibrational degrees of freedom and low energy electron-hole excitations [9, 10]), and of published transport data [11, 12], we will develop a qualitative model for the electronic structure of the TM mono-silicides [13]. This framework provides a basis for understanding the observed range of chemical stability of these compounds (from CrSi to NiSi), and the properties of FeSi.

In chapter 3 we will concentrate on CuGeO_3 which can be described as a quasi one-dimensional (1D) system due to the presence of weakly-coupled 1D CuO_2 chains, running parallel to each other. Because each Cu^{2+} ion has spin 1/2 and the exchange between these local moments is antiferromagnetic (AF), the CuO_2 chains can be regarded as 1D AF $S = 1/2$ -Heisenberg-spin chains. In CuGeO_3 , for temperatures lower than 14 K, electron-electron correlations and the low dimensionality give rise to a fascinating phenomenon, namely, the spin-Peierls (SP) phase transition [14, 15]: A lattice distortion that occurs together with the formation of a nonmagnetic ground state ($S = 0$), and the opening of a finite energy gap in the magnetic excitation spectrum. We will discuss the temperature dependent optical data for pure and doped CuGeO_3 and, in particular, the phonon spectra, seeking for optical vibrational modes activated by the SP phase transition [16, 17]. We will show that, following the temperature dependence of these modes, we can determine the second order character of the phase transition and study the effect of doping on T_{SP} : The

substitution of Ge with Si will turn out to be three times more efficient, than the one of Cu with Mg, in reducing T_{SP} . This result will be discussed in relation to the difference, between Mg and Si doping, in affecting the magnetism of the system [18].

In chapter 4 and 5 we will devote our attention to α' - NaV_2O_5 , another quasi 1D inorganic compound which, after CuGeO_3 , has been attracting the attention of the scientific community working on low-dimensional spin systems, in general, and on the SP phenomenon, in particular. In fact, in 1996 the SP picture was proposed to explain the low temperature properties of α' - NaV_2O_5 , with a transition temperature $T_{\text{SP}} = 34$ K [19]. As in the case of CuGeO_3 , by analyzing the optically allowed phonons at various temperatures below and above the phase transition [20], we will show that, consistently with the proposed SP picture, a second-order change to a larger unit cell takes place below 34 K (chapter 5). On the other hand, on the basis of recently reported specific heat measurements in high magnetic field [21], the interpretation of the phase transition in α' - NaV_2O_5 is still controversial. We will see that an even more basic problem is the determination of crystal structure and symmetry of the electronic configuration, for α' - NaV_2O_5 in the high temperature phase. In fact, the analysis of x-ray diffraction measurements [22] and optical phonon spectra suggests that the symmetry of this compound, at room temperature, is better described by the centrosymmetric space group $Pm\bar{m}n$ than by the noncentrosymmetric $P2_1mn$ proposed in the 1970's [23]. On the other hand, the intensities and polarization dependence of the electronic excitations detected in the optical spectra are not understandable in terms of the centrosymmetric space group (chapter 5). We will show that a consistent interpretation of both x-ray diffraction results and optical conductivity data requires a charge disproportionated electronic ground-state at least on a local scale, i.e., without any long range order [24]. It will then be possible to interpret the optical conductivity on the basis of the *Charged Magnon Model* developed in chapter 4, and show that the presence of only one d electron per two V ions, along with the broken symmetry of the ground-state, gives rise to a fascinating behavior of the spin flips in α' - NaV_2O_5 : Spin-flip excitations carry a finite electric dipole moment, which is responsible for the detection of *charged bi-magnons* in the optical spectra, i.e., direct two-magnon optical absorption processes [20].

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