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$\begin{array}{c} \mbox{Lattice Dynamics of VO}_2 \ \mbox{Above the} \\ \ \mbox{Metal-Insulator Transition} \end{array}$

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Abstract

In this thesis a study of the lattice dynamics of vanadium dioxide by means of Inelastic X-ray Scattering (IXS) and Thermal Diffuse Scattering (TDS) is presented. The project was conducted at the European Synchrotron Radiation Facility in Grenoble. The main measurements were performed at beam line ID28 using the IXS technique, while the TDS results were obtained at beam line ID23.

The study of lattice dynamics allows to obtain information about the collective excitations (phonons) in a periodic lattice. Thanks to quantum mechanics, a phonon can be seen as a quasiparticle, representing an excited state of the mode of vibrations of a crystal. Knowing the phonon dispersion allows to access various material properties, such as sound velocities, elastic constants, phonon-phonon interactions, electron phonon-interactions and dynamical instabilities. For example, phonons are responsible for the spectacular phenomenon of superconductivity: electron-phonon coupling is the driving mechanism of this process, allowing to explain the behaviour of BCS superconductors.

Vanadium dioxide exhibits a Metal-Insulator Transition (MIT) at about 340 K, and this material has been widely studied along the past decades, trying to understand the mechanism driving this transformation. Here the low temperature phase is the insulating phase, while the high temperature one is metallic. The VO₂ is neither the only vanadium oxide, nor the only transition metal oxide showing this kind of property, but it is the only one being characterized by a transition temperature so close to room temperature. In addition to being interesting from a fundamental point of view, VO₂ has recently drawn a lot of attention since it offers a novel route to novel electronic and photonic applications.

Together with the MIT, a Structural Phase Transition (SPT) takes place, suggesting that the lattice dynamics can play a crucial role across the transition. One possible model which allows to explain the MIT process is known as Peierls transition: this model attributes the radical transformation of this material to electron-lattice interactions. Nevertheless, the MIT process can also originate from electron-electron interactions, and this time the mechanism is referred to as Mott (or Mott-Hubbard) transition. Different theoretical models and a lot of experimental results have been presented to support both the explanations, but an accurate description of lattice dynamics was still missing.

The aim of this work is to provide a thorough description of the lattice dynamics of VO_2 in the metallic phase, thus above the transition temperature. Combining the IXS and TDS techniques, it is possible to obtain direct dispersion relation measurements and diffuse scattering maps. These results give a good picture of the phonon energy (and intensity) landscape, highlighting the role that lattice dynamics plays within the metal-insulator transition.

The experimental results show the undeniable presence of lattice instabilities in the high temperature phase of vanadium dioxide. Indeed, low energy acoustic phonons are present in more than one high-symmetry direction of the Brillouin zone. From these results it is evident that electron-lattice interactions play an important role across the MIT, but, of course, the results themselves do not allow to exclude the presence of electron correlations.

Sommario

In questa tesi è presentato lo studio della dinamica vibrazionale del diossido di vanadio (VO₂), grazie all'utilizzo delle tecniche sperimentali dell'*Inelastic X-ray Scattering* (IXS) e del *Thermal Diffuse Scattering* (TDS). Il progetto è stato svolto presso l'European Synchrotron Radiation Facility (ESRF) di Grenoble, in particolare all'interno del gruppo di ID28, beamline specializzata nell'utilizzo della tecnica IXS per lo studio della dinamica vibrazionale. Le misure di scattering diffuso, invece, sono state realizzate nella beamline ID23.

Lo studio della dinamica vibrazionale permette di ottenere informazioni inerenti alle eccitazioni collettive (fononi) di un reticolo periodico. Grazie alla meccanica quantistica, è possibile descrivere un fonone come una quasi-particella, che rappresenta uno stato eccitato dei modi vibrazionali di un cristallo. Le relazioni di dispersione dei fononi costituiscono un importante mezzo per conoscere svariate proprietà di un materiale, ed alcune di queste sono: velocità del suono, costanti elastiche interazioni fonone-fonone, interazioni elettrone-fonone e instabilità del reticolo. Uno dei fenomeni più famosi nel quale i fononi sono coinvolti è la superconduttività: infatti, l'interazione elettrone-fonone è in grado di spiegare il comportamento dei superconduttori che rientrano nella teoria BCS (tradizionali superconduttori a bassa temperatura di transizione).

Il VO₂ è stato ampiamente studiato durante gli ultimi decenni, principalmente grazie alla sua interessante caratteristica di mostrare una transizione metallo-isolante (MIT) alla temperatura di circa 340 K, dove la fase a più basse temperature è quella isolante, mentre quella ad alte temperature è la fase metallica. Il VO₂ non è né l'unico ossido di vanadio, né l'unico ossido di metalli di transizione a mostrare una MIT, ma è l'unico tra questi a possedere una temperatura di transizione così vicina alla temperatura ambiente. Inoltre, il diossido di vanadio sta recentemente attirando ulteriori attenzioni grazie a diverse applicazioni tecnologiche nelle quali può essere impiegato,

sia nel campo dell'elettronica che della fotonica.

Ulteriore caratteristica di questo materiale, è la presenza di un cambiamento nella struttura reticolare in concomitanza con la transizione metallo-isolante. Questo fatto porta a pensare che la dinamica vibrazionale possa giocare un ruolo importante nella MIT, grazie a interazioni elettrone-fonone che porterebbero ad una transizione ben descritta nel modello proposto da Peierls. Ciononostante, un secondo meccanismo è stato proposto per spiegare il processo di MIT: questo è il modello di Mott (o Mott-Hubbard), e si basa sull'idea di una transizione guidata da interazioni elettrone-elettrone. Molti risultati sperimentali sono stati presentati a favore di entrambi i modelli proposti, dividendo la comunità scientifica per lungo tempo.

Il principale scopo di questo lavoro è quello di applicare le tecniche sopra citate, di IXS e TDS, in modo tale da fornire una accurata desrizione della dinamica vibrazionale del diossido di vanadio nella fase metallica. La combinazione di queste due tecniche sperimentali, permette di ottenere misure dirette di relazioni di dispersione e mappe di scattering diffuso. Da queste è possibile ricavare importanti informazioni inerenti al ruolo della dinamica vibrazionale nel processo di transizione metallo-isolante.

I risultati sperimentali mostrano in modo innegabile la presenza di instabilità reticolari nella fase metallica del VO_2 . Fononi acustici caratterizzati da basse energie sono presenti in più di una direzione di alta simmetria all'interno della zona di Brillouin. Risulta quindi evidente da questi risultati che interazioni elettrone-fonone sono presenti all'interno di questo sistema, prendendo parte al processo di MIT, ma ciò non permette di escludere la presenza di correlazioni elettroniche.

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Chapter 1

Theoretical Basis

1.1 Introduction

It is useful to start with a brief overview concerning the theoretical basis, in order to get familiar with the standard formalism of lattice dynamics. The study of lattice vibrations is very important, since it can give a lot of information about a material properties, such as sound velocities, elastic constants, interatomic force constants, phonon-phonon interactions, phonon-electron coupling and dynamical instabilities. A lot of references exist dealing with these topics, which provide different approaches for describing the formalism (for example [1, 2, 3]). Here we follow the formalism of Willis and Prior [4].

The phrases 'lattice dynamics' or 'lattice vibrations' refer to the collective modes, which are modes of vibrations, of the entire crystalline solid. The most important information regarding the lattice dynamics are contained within the dynamical matrix; to get there, we start by considering the simplified problem of the vibration of atoms in an isolated molecule.

Suppose our molecule is composed by n atoms, then 3n coordinate are needed to describe their displacements from the equilibrium position. If the symbol κ is used to label each atom, then we may exploit a single 3n-vector \mathbf{u} (with 3n components) to represent the atomic displacements in the entire molecule. In terms of matrix notation, \mathbf{u} vector can be seen as a $3n \times 1$ column matrix; to show that in a compact notation we can use the transposed quantity \mathbf{u}^{T}

$$\mathbf{u}^{T} = (u_{1}(1) \, u_{2}(1) \, u_{3}(1) \dots u_{1}(n) \, u_{2}(n) \, u_{3}(n)), \tag{1.1.1}$$

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where $u_{\alpha}(\kappa)$ represents the components of the displacement of the κ -th atom, along the three Cartesian axes α ($\alpha = 1, 2, 3$).

Now we can proceed introducing the interatomic forces, which must be functions of the atomic displacement. Let's assume that the force on atom κ arising from its interaction with another atom κ ' can be written as a simple linear function of the displacements

$$\mathbf{F}(\kappa) = -\mathbf{\Phi}(\kappa\kappa')\,\mathbf{u}(\kappa'). \tag{1.1.2}$$

This formula represents a set of three linear equations, and it tells us that the force exerted on atom κ in any arbitrary direction, is proportional to the displacement of atom κ' in any other arbitrary direction. Moreover, the quantity $\Phi(\kappa\kappa')$ is the 3×3 force-constant matrix of the form

$$\mathbf{\Phi}(\kappa\kappa') = \begin{pmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} \end{pmatrix},$$
(1.1.3)

where the subscripts refer to axis directions; for example, the element $\Phi_{32}(\kappa\kappa')$ is the negative of the force on atom κ in the z-direction, when atom κ' is displaced along the y-direction by one unit. These force-constant matrices can also be related directly to the potential energy of the whole molecule, in fact, writing the Taylor expansion of the potential energy in the atomic displacement gives

$$2V = 2V_0 + 2\sum_{\kappa\alpha} \left(\frac{\partial V}{\partial u_{\alpha}(\kappa)}\right)_0 u_{\alpha}(\kappa) + \sum_{\kappa\alpha} \sum_{\kappa'\alpha'} \left(\frac{\partial^2 V}{\partial u_{\alpha}(\kappa) \partial u_{\alpha'}(\kappa')}\right)_0 u_{\alpha}(\kappa) u_{\alpha'}(\kappa') + \dots, \qquad (1.1.4)$$

where α and α' both refer to the three axes, and the 0 outside each derivative, means that they have to be evaluated at the equilibrium atomic positions (null displacement). It is obvious that the energy is at its minimum value when all the atoms are at their equilibrium positions, so that all the first derivative of terms in Equation 1.1.4 are zero. Now it is possible to introduce two more approximation, which allow to simplify a lot the previous expression:

1. zero-energy is chosen so that the energy of the equilibrium configuration is zero $(V_0 = 0);$

2. harmonic approximation allows to cut the Taylor expansion at the second-order derivative of the potential energy; the physical meaning of this approximation is that the atoms of the system vibrate with a simple harmonic motion.

Thus, noticing that the α component of the force acting on atom κ when it is moved from its equilibrium position is $-\partial V/\partial u_{\alpha}(\kappa)$, and exploiting a simplified form of Equation 1.1.4, we can get

$$F_{\alpha}(\kappa) = -\left(\frac{\partial^2 V}{\partial u_{\alpha}(\kappa) \partial u_{\alpha'}(\kappa')}\right)_0 u_{\alpha'}(\kappa'), \qquad (1.1.5)$$

which represents the interaction of κ with just one of the others κ' atoms inside the molecule. This way, it is straightforward to write

$$\Phi_{\alpha\alpha'}(\kappa\kappa') = \left(\frac{\partial^2 V}{\partial u_{\alpha}(\kappa) \,\partial u_{\alpha'}(\kappa')}\right)_0,\tag{1.1.6}$$

thanks to Equation 1.1.2.

Until now we have used a very powerful object without even talking about it, but now it is necessary to introduce it: this is the adiabatic (or Born-Oppenheimer) approximation. This model is based on the fact that the mass of nuclei is much bigger that the mass of an electron. Thus, it is possible to decouple the nuclei and electrons motions, and, more generally, it allows to split the whole complex system into an electronic and a nuclear part to be solved separately. Together with the harmonic approximation, they represent the starting point to talk about molecular (and lattice) vibrations:

- thanks to the harmonic approximation we can write the potential energy in the quadratic form, and force as a linear function of the displacements (see Equation 1.1.2);
- adiabatic approximation allows us to write the potential energy without the specific involvement of the electron coordinates. This means that the electrons instantaneously take up a configuration appropriate to the displaced nuclei, being the electron dynamics much faster than the nuclei dynamics because of the masses involved.

1.2 Equations of motion

Newton's classical equations of motion can be used to describe the displacement of atoms out of their equilibrium positions, so that motion of atom κ of mass $m(\kappa)$ can be written in the form

$$m(\kappa) \ddot{\mathbf{u}}(\kappa, t) = -\sum_{\kappa'} \boldsymbol{\Phi}(\kappa \kappa') \, \mathbf{u}(\kappa', t), \qquad (1.2.1)$$

which represents three equations, one for each Cartesian direction. Since we are talking about atomic shifts from their equilibrium positions, it is valid to assume an oscillatory solution, like

$$\mathbf{u}(\kappa, t) = \mathbf{U}(\kappa) e^{-i\omega t}, \qquad (1.2.2)$$

where ω is the frequency of vibration, and **U**(κ) represents the amplitude of vibration of atom κ . Substituting this possible solution in Equation 1.2.1 we get

$$m(\kappa)\,\omega^2\,\mathbf{U}(\kappa) = \sum_{\kappa'} \boldsymbol{\Phi}(\kappa\kappa')\,\mathbf{U}(\kappa'). \tag{1.2.3}$$

Thus, if the summation over κ runs over all n atoms, Equation 1.2.3 represents a set of 3n equations. A compact notation is needed to represent this problem in a simple way; this is done by means of a matrix notation. The displacements of all atoms are contained in the $3n \times 1$ column matrix \mathbf{U}_0 , and a 'mass matrix' is also introduced, which is a simple $3n \times 3n$ diagonal matrix \mathbf{m} . The last step consists in assembling all the $3 \times 3 \Phi(\kappa \kappa')$ matrices as blocks of a big $3n \times 3n$ matrix called \mathbf{M}_0 . Here the subscript 0 is used to indicate that a particular matrix is not mass-adjusted. Using this compact notation we can rewrite Equation 1.2.3 in the succinct form

$$\omega^2 \operatorname{\mathbf{m}} \mathbf{U}_0 = \mathbf{M}_0 \operatorname{\mathbf{U}}_0, \tag{1.2.4}$$

where we still miss the mass-adjustment to get to a standard eigenvalue problem. Thus, multiplying both sides by $\mathbf{m}^{-\frac{1}{2}}$ we reach \mathbf{U} and \mathbf{M} , the mass-adjusted forms of \mathbf{U}_0 and \mathbf{M}_0 respectively. This way, the final shape of our problem becomes

$$\omega^2 \mathbf{U} = \mathbf{M} \mathbf{U}, \tag{1.2.5}$$

where **M** is a real symmetrical $3n \times 3n$ square matrix. Using standard matrix methods, it is possible to reach the characteristic equation of the matrix **M**

$$det(\mathbf{M} - \omega^2 \mathbf{I}) = 0, \qquad (1.2.6)$$

where **I** is a $3n \times 3n$ unit matrix. Thus, because of the dimensions of our system (a molecule in this case), we get an equation of the 3n-th degree, whose roots give 3n eigenvalues, which are the values of the squared frequency ω^2 . We are sure that the eigenvalues are real, thanks to the fact that matrix **M** is real symmetric; moreover, we need all the eigenvalues to be positive in order to have dynamical stability of our system, for the set of force constants employed. Of course, by substituting the eigenvalues inside Equation 1.2.5, we get the set of eigenvectors; each eigenvalue has its correspondent eigenvector describing the relative displacement of the atoms vibrating with that particular frequency. It is convenient at this point, to introduce a new symbol, j (with j = 1, 2, 3, ..., 3n), in order to label the eigenvalues and eigenvectors. Thanks to the orthonormality condition on the eigenvectors, it is possible to picture them as a set of independent harmonic oscillators; these 3n independent modes are known as the NORMAL MODES OF VIBRATION of our system. In this simple picture, matrix **M** is the one containing all the information about our system, that is the molecule; to reach the dynamical matrix we need to do some more steps.

1.3 Born - von Karman theory

Now we will switch the concepts shown above from the molecular description to the more complex crystalline solid structure. The starting point to do so, is the theory introduced by Born and von Karman, which carry in two new ideas of fundamental importance:

- 1. we can suppose our crystal to be finite, but unbounded, an assumption also known as the cyclic boundary conditions. We can imagine our crystal to be sufficiently large so that the atoms at the surface comprise a very small portion of the total; this way, the cyclic boundary conditions allow us to neglect completely the surface. Let's picture a crystal with N_1 unit cells along a particular axis: the conditions state that the N_1 -th cell is linked around to the first cell in a loop (and so the same for the other two directions);
- 2. the vibrations are no longer considered as simple oscillating stationary modes,

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but as travelling waves running through the whole crystal.

These two concepts bring us to introduce a new kind of solution of the equations of motion (replacing Equation 1.2.2), with the following shape

$$\mathbf{u}(\kappa l, t) = \mathbf{U}(\kappa | \mathbf{q}) \exp\left[i\left(\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega(\mathbf{q})t + \phi(\kappa | \mathbf{q})\right)\right], \quad (1.3.1)$$

where it is important to highlight that now κ refers to a particular atom in the unit cell, and l labels a unit cell. Even if the formalism for the description remains the same, there is a different behaviour of our system: the equilibrium position of one atom is $\mathbf{r}(\kappa l)$, and its displacement $\mathbf{u}(\kappa l, t)$ depends on the wave vector \mathbf{q} of the travelling wave. The vector $\mathbf{U}(\kappa | \mathbf{q})$ expresses the amplitude and the direction of the displacement of atom κ , as produced by the travelling wave (with wave vector \mathbf{q}); it is important to notice that this vector is the same for all unit cells due to Bloch's theorem, which states that for corresponding atoms in different unit cells, the movements are identical as regards their amplitude and direction, with the only difference being the phase. Let's suppose to have a crystal with N unit cells and n atoms per unit cell, for a total number of 3nN atoms: thanks to Bloch's theorem our problem can be reduced from studying 3nN equations (one for each atom), to study just 3n equations of motion, restricting our attention to just the atoms within a unit cell. This means that the n atoms within a unit cell play the same role of the n atoms of a molecule. Now, because of the wave picture, we can find two different configurations:

- 1. longitudinal waves: the atomic displacements are parallel to the propagation direction of the wave itself (so they are parallel to **q**);
- 2. transverse waves: $\mathbf{U}(\kappa \mid \mathbf{q})$ is perpendicular to \mathbf{q} .

We note from Equation 1.3.1 that the frequency is a function of the wave vector, and this dependence of ω on \mathbf{q} , $\omega(\mathbf{q})$, gives the dispersion relation for the propagation direction defined by \mathbf{q} . Dispersion relations give direct insights about the vibrational energies across the reciprocal space, highlighting some important features like lattice instabilities and possible electron-phonon interactions. The only term left is the phase factor $\phi(\kappa | \mathbf{q})$, which is usually embedded inside the vector \mathbf{U} in order to rewrite the last equation as

$$\mathbf{u}(\kappa l, t) = \mathbf{U}(\kappa | \mathbf{q}) \exp\left[i\left(\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega(\mathbf{q})t\right)\right], \qquad (1.3.2)$$

where the vector $\mathbf{U}(\kappa \mid \mathbf{q})$ is now complex.

From this new starting point, it is possible to develop the formalism for lattice dynamics following the same steps introduced above. The equations of motion for the κ -th atom in the *l*-th unit cell are

$$m(\kappa) \ddot{\mathbf{u}}(\kappa l, t) = -\sum_{\kappa' l'} \mathbf{\Phi} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} \mathbf{u}(\kappa' l', t),$$
(1.3.3)

where the elements of the force-constant matrix are now related to the potential energy of the crystal, by the same expression as before (just adding the unit cell index l in the formula). Thus, substituting Equation 1.3.2 inside the equations of motion, and applying the mass-adjustment, we can get the eigenvalue equation

$$\omega^2 \mathbf{U} = \mathbf{D} \mathbf{U}, \tag{1.3.4}$$

where U is the mass-adjusted displacement vector as before, defined by the relation $\mathbf{U} = \mathbf{m}^{\frac{1}{2}} \mathbf{U}_0$. Here **m** is the mass matrix previously defined, and \mathbf{U}_0 is the column matrix assembled from the elements of the $\mathbf{U}(\kappa | \mathbf{q})$

$$\mathbf{U}_{0}^{T}(\mathbf{q}) = (U_{1}(1|\mathbf{q}) U_{2}(1|\mathbf{q}) U_{3}(1|\mathbf{q}) \dots U_{1}(n|\mathbf{q}) U_{2}(n|\mathbf{q}) U_{3}(n|\mathbf{q})).$$
(1.3.5)

Finally, $\mathbf{D}(\mathbf{q})$ is the mass-adjusted $3n \times 3n$ dynamical matrix defined by

$$\mathbf{D} = \mathbf{m}^{-\frac{1}{2}} \,\mathbf{D}_0 \,\mathbf{m}^{-\frac{1}{2}},\tag{1.3.6}$$

and a typical element has the following shape

$$D_{\alpha\alpha'}(\kappa\kappa'|\mathbf{q}) = \left(m(\kappa)\,m(\kappa')\right)^{-\frac{1}{2}}\,\sum_{l'}\Phi_{\alpha\alpha'}\left(\begin{array}{cc}\kappa & \kappa'\\ 0 & l'\end{array}\right)\,\exp\left[i\mathbf{q}\cdot(\mathbf{r}(\kappa'l')-\mathbf{r}(\kappa0))\right],\quad(1.3.7)$$

where the interactions expressed in the last formula are between atom κ within the unit cell 0, and all the atoms κ' inside every unit cell of the crystal. Thus, the dynamical matrix is the (mass-reduced) Fourier transform of the force-constant matrix. The last exponential term represents the phase factor, which rise from the different positions of the atoms we are considering; because of it, the dynamical matrix results to be complex, unless every atom is at a center of symmetry. Nevertheless, the **D** matrix is Hermitian by construction, meaning that $\mathbf{D} = (\mathbf{D}^*)^T$, and thanks to this the eigenvalues of Equation 1.3.4 are always real, but the eigenvectors can be complex anyway. As before, we can use the symbol j to label the eigenvalues (j = 1, 2, ..., 3n), but it

now refers to a branch of the dispersion relation. Each branch contains N frequencies corresponding to the N **q**-vectors in the Brillouin zone. Because of this new representation, for each q-vector in the zone there is a normal mode frequency $\omega_j(\mathbf{q})$, with a corresponding eigenvector. As previously mentioned about the simplified system concerning a molecule vibrations, the eigenvectors $\mathbf{U}(j\mathbf{q})$ just give the relative amplitude of the atomic vibrations; it is convenient, therefore, to use normalized eigenvectors $\mathbf{e}(j\mathbf{q})$ such that

$$\sum_{\alpha\kappa} e_{\alpha}^{*}(\kappa|j\mathbf{q}) e(\kappa|j'\mathbf{q}) = \delta_{jj'} .$$
(1.3.8)

Consequently, the column matrices $\mathbf{U}(j\mathbf{q})$ become

$$\mathbf{U}(j\mathbf{q}) = |A(j\mathbf{q})| \ \mathbf{e}(j\mathbf{q}), \tag{1.3.9}$$

where $|A(j\mathbf{q})|$ is a scalar constant, characterizing the amplitude of excitation of the mode $(j\mathbf{q})$. This way the eigenvector $\mathbf{e}(j\mathbf{q})$ is a column matrix like this

$$\mathbf{e}^{T}(j\mathbf{q}) = (e_{1}(1|j\mathbf{q}) e_{2}(1|j\mathbf{q}) e_{3}(1|j\mathbf{q}) \dots e_{1}(n|j\mathbf{q}) e_{2}(n|j\mathbf{q}) e_{3}(n|j\mathbf{q})),$$
(1.3.10)

where a single 3×1 component of $\mathbf{e}(j\mathbf{q})$

$$\mathbf{e}(\kappa|j\mathbf{q}) = \begin{pmatrix} e_1(\kappa|j\mathbf{q}) \\ e_2(\kappa|j\mathbf{q}) \\ e_3(\kappa|j\mathbf{q}) \end{pmatrix}$$
(1.3.11)

is known as polarization vector of atom κ , when vibrating in mode (*j***q**). Using this new notation, we get to the final equation

$$\omega_i^2(\mathbf{q}) \, \mathbf{e}(j\mathbf{q}) = \mathbf{D}(\mathbf{q}) \, \mathbf{e}(j\mathbf{q}) \tag{1.3.12}$$

that has to be solved in order to determine the 3n eigenvalues and the corresponding eigenvectors.

To end this theoretical introduction, we can very briefly highlight the most important results:

- through the square root of the eigenvalues, we get the vibrational frequency (and so the energy) associated to each vibrational mode;
- the eigenvectors correspondent to each eigenvalue, give us the pattern of atomic

displacements belonging to each vibrational mode;

• the dynamical matrix **D**(**q**) contains the complete information of the lattice dynamics of our system.

Chapter 2

Experimental Techniques

In this thesis, two different experimental techniques are going to be used in order to study the lattice dynamics of vanadium dioxide. The two techniques are the Inelastic X-ray Scattering (IXS) and the Thermal Diffuse scattering (TDS). Here they are going to be introduced, starting from a general description, then going deeper in order to highlight the power of both these tools.

2.1 Inelastic X-ray Scattering

This is an X-ray spectroscopy technique in which high energy, X-ray photons are inelastically scattered off matter. It is a photon-in photon-out process, where both the energy and momentum change of the scattered photon are measured. Generally speaking, it is a versatile technique, since choosing the right energy change range it is possible to study the different elementary excitations in condensed matter (see Figure 2.1.1): starting from the low energy excitations, phonons and magnons can be inspected (~1-100 meV), then there are valence electron excitations and plasmons (~1-10 eV) and finally the core electron excitations, up to 1 keV. In this work we exploit the IXS technique to study phonon vibrations, thus the order of magnitude we are interested in for the energy loss is 1 meV. Comparing the very small energy change that needs to be detected with the energy of the incident photon which is around 10 keV, the resulting relative energy resolution needed is at least $\frac{\Delta E}{E} = 10^{-7}$. This is the reason why such experiments are so challenging, and they cannot be accomplished using a conventional X-ray tube because of its intrinsic characteristics. Indeed, before the advent of high intensity X-rays produced thanks to the modern synchrotrons (in the



Figure 2.1.1: Schematic representation of the elementary excitations being studied with the inelastic X-ray scattering technique.

1990's), the inelastic neutron scattering method (INS) was the leading technique to obtain direct measurements of dispersion curves, since the 1960's. Neutrons fit very well for this kind of application, thanks to their properties:

- the study of phonon vibrations requires an incident wavelength of the order of the interparticle distances, and neutrons with $\lambda \sim 0.1 nm$ have an energy o about 100 meV, which is close enough to typical phonon energies;
- the neutron-nucleus scattering cross-section is small enough to allow for a large penetration depth.

Other experimental methods that allow to study the vibrational properties of a material (with energy resolution up to 10^{-8} eV) are the Brillouin and Raman scattering, but they can only determine acoustic and optical modes, respectively, with a momentum transfer limited to an area close to the center of the Brillouin zone. Thanks to the appearance of third generation synchrotron radiation sources, providing very high photon flux and brilliance, direct measurements of phonon dispersions were possible. By the end of the 1990's the technique of inelastic X-ray scattering for phonons reached its full maturity, allowing to reach an energy resolution of 1.5 meV. Moreover, X-rays has some advantages with respect to neutrons:

• X-rays allow to successfully study elements with a large incoherent cross-section,

which do not permit to get good results with neutrons;

• INS experiments typically require volumes of several mm^3 , while IXS measurements can be successful on samples of very small sizes, until $10^{-5} mm^3$, thus consenting to study materials only available in very small quantities and the investigation of materials in extreme thermodynamic conditions (for example very high pressure).

2.1.1 The Scattering Process

The geometry of a general inelastic scattering process is displayed in Figure 2.1.2. Here the incident monochromatic beam possesses well known wavevector \mathbf{k}_i , energy



Figure 2.1.2: Schematic picture of a scattering process [6].

 E_i and polarization unit vector \mathbf{e}_i ; after hitting the target, it is scattered into the solid angle element $d\Omega$, and the angle 2θ is known as scattering angle. The scattered beam is defined by the wavevector \mathbf{k}_f , the energy E_f and the polarization vector \mathbf{e}_f , thus, thanks to the conservation of both energy and momentum, it is possible to extract information about the momentum and energy transfer

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \,, \tag{2.1.1}$$

$$E = E_i - E_f \,. \tag{2.1.2}$$

In these two formulae E is the energy transferred to the system in order to create (or annihilate) a phonon, and **Q** is referred to as the scattering vector. In the frame of IXS for phonons, the energy losses (or gain) associated with phonon excitations are always much smaller than the incident photon energy ($E \ll E_i$), and this allows to simplify the

expression for the scattering vector like this

$$Q = 2k_i \sin(\theta), \qquad (2.1.3)$$

since the relation between energy and momentum for photons is $E(k) = \hbar c k$. Here it is possible to highlight that for IXS, at a given momentum transfer, there are no limitations in the energy transfer for phonon excitations, in contrast to INS where energy and momentum transfer are strongly coupled.

2.1.2 Scattering Cross-Section

The physical quantity that can be experimentally measured is the double differential cross-section

$$\frac{d^2\sigma}{d\Omega \, dE_f}\,,\tag{2.1.4}$$

and it is proportional to the number of incident probe particles (photons for IXS) scattered into the solid angle element $d\Omega$ within the energy range E_f and $E_f + dE_f$. Before proceeding with a detailed description of the cross-section, one needs to introduce the Hamiltonian that describes the system under study. In order to model the electronphoton interaction in a scattering process, within the weak relativistic limit, a four terms Hamiltonian is used [5]. Now, it is possible to neglect resonance phenomena close to X-ray absorption thresholds and even weaker magnetic couplings, just leaving the term arising from the Thomson interaction Hamiltonian

$$H_{Th} = \frac{1}{2} r_0 \sum_{j} \mathbf{A}^2(\mathbf{r}_j, t) , \qquad (2.1.5)$$

where $r_0 = \frac{e^2}{m_e c^2}$ is the classical electron radius and $\mathbf{A}^2(\mathbf{r}_j, \mathbf{t})$ is the vector potential of the electromagnetic field in the \mathbf{r}_j coordinate of the *j*-th electron, and the sum extend over all electrons inside the system. Starting from the situation previously introduced for the scattering process, the probability to transmit a plane-wave state $|\mathbf{k}_i\rangle$ to the plane-wave state $|\mathbf{k}_f\rangle$ is given by the Fermi's Golden Rule, thanks to the application of the first order perturbation theory. By using the Dirac bra-ket notation, it is possible to express the initial and final states describing the electron system of the sample as $|I\rangle$ and $|F\rangle$, respectively. Combining all the ingredients (see [6, 7]), the scattering cross-section can be expressed as

$$\frac{d^2\sigma}{d\Omega dE_f} = r_0^2 (\mathbf{e}_f \cdot \mathbf{e}_i)^2 \left(\frac{k_f}{k_i}\right) \sum_{I,F} P_I \left| \left\langle F \left| \sum_j e^{i\mathbf{Q}\mathbf{r}_j} \right| I \right\rangle \right|^2 \delta(E + E_f - E_i) .$$
(2.1.6)

At this point, a couple of considerations can be introduced; the first is the validity of the adiabatic approximation. This allows separating the general quantum state $|S\rangle$ into the product of an electronic and nuclear part: $|S\rangle = |S_e\rangle |S_n\rangle$. This approximation is particularly suitable when the exchanged energies are small with respect to the electron excitation energies, and it is just the case for phonons. The contribution to the total scattering coming from the valence electrons close to the Fermi level is small compared to the contribution coming from the core electrons. Thus, it is possible to assume that the electronic part of the total wavefunction is not changed by the scattering process, and therefore the difference between the initial and final state is substantially due to the excitations of the ion system. This way, it is possible to rewrite the second part of Equation 2.1.6, starting from the first summation

$$\sum_{I_n,F_n} P_{I_n} \left| \left\langle F_n \left| \sum_k f_k(Q) e^{i\mathbf{QR}_k} \right| I_n \right\rangle \right|^2 \delta(E + E_f - E_i), \qquad (2.1.7)$$

where $f_k(Q)$ is the atomic form factor of the atom k, representing the Fourier transform of the electron density, and \mathbf{R}_k is the position vector of the k-th atom. Since the scattering process occurs from the electronic cloud of the atom, f(Q) is equal to the atomic number Z for $Q \to 0$ and it decays almost exponentially with increasing momentum transfer. The sum k extends over all atoms of the system. Thus, the differential cross-section can be separated into two parts

$$\frac{d^2\sigma}{d\Omega dE_f} = \left(\frac{d\sigma}{d\Omega}\right)_{Th} \cdot S(\mathbf{Q}, E) \,. \tag{2.1.8}$$

The first factor is known as Thomson scattering cross-section

$$\left(\frac{d\sigma}{d\Omega}\right)_{Th} = r_0^2 (\mathbf{e}_f \cdot \mathbf{e}_i)^2 \left(\frac{k_f}{k_i}\right) , \qquad (2.1.9)$$

and it describes the coupling of the electromagnetic field of the incident photons, to the electrons of the system. In this case, it results to be weak, since r_0^2 is of the order of 10^{-25} cm², and because of the very small energy transfer with respect to the energy

of the incoming photons (more than 10 keV), the term $\binom{k_f}{k_i}$ is about equal to one. Proceeding with the second factor, that is displayed in Equation 2.1.7, it is known as scattering function S(**Q**, E). The scattering function describes the properties of the sample in the absence of the perturbing probe, and it gives direct information about the dynamics of the system from an inelastic scattering experiments. In order to switch from X-ray to neutron cross-section, the Thomson factor and the atomic form factor have to be replaced by the coherent neutron scattering length *b* of the element under study. Thanks to the adiabatic approximation previously introduced, the electrons are expected to follow the motions of the nuclei instantaneously, therefore phonons, which represents low frequency movements of the nuclei, will cause electron charge density variations, which can be directly observed by inelastic X-ray scattering. Indeed, the scattering function S(**Q**, E) can be expressed as the time and space Fourier transform of the density-density correlation function

$$S(\mathbf{Q}, E) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt \, e^{-\frac{iEt}{\hbar}} \int d\mathbf{r} \, e^{i\mathbf{Q}\cdot\mathbf{r}} \left\langle \rho(\mathbf{r}', t=0) \, \rho(\mathbf{r}'+\mathbf{r}, t) \right\rangle \,, \tag{2.1.10}$$

with

$$\rho(\mathbf{r}, t) \triangleq \sum_{j} \delta(\mathbf{r} - \mathbf{r}_{j}(t)) \,. \tag{2.1.11}$$

Equation 2.1.10 contains information about the particle fluctuation inside the target system, in different states at different times. Here, N is the number of particle in the system, and $\langle \rho(\mathbf{r}', t = 0) \rho(\mathbf{r}' + \mathbf{r}, t) \rangle$ is the time dependent two-particle pair correlation function, where the $\langle ... \rangle$ denotes the ground state expectation value of the density operator product. The summation *j* (Equation 2.1.11) runs over all the target particle of the system. In the classical limit, the pair correlation function gives the probability of finding a particle belonging to the target at time *t* and at $\mathbf{r}' + \mathbf{r}$, if there was any particle at time t = 0 and at the position \mathbf{r}' . Now, in the case of single phonon studies for a single crystal sample, and within the harmonic approximation, the scattering function can be further divided into two factors

$$S(\mathbf{Q}, E) = \sum_{j} G(\mathbf{Q}, j) F(E, T, \mathbf{Q}, j).$$
 (2.1.12)

Here, the first term is the dynamical structure factor

$$G(\mathbf{Q}, j) = \left| \sum_{k} M_{k}^{-\frac{1}{2}} f_{k}(Q) \left[\mathbf{e}_{k}^{j}(\mathbf{q}) \cdot \mathbf{Q} \right] e^{i\mathbf{Q}\cdot\mathbf{r}_{k}} e^{-W_{k}} \right|^{2}, \qquad (2.1.13)$$

where M_k is the mass of atom k, e^{-W_k} is the Debye-Waller factor, \mathbf{r}_k is the position of atom k in the unit cell and the summation k runs over all atoms inside the unit cell. The vector $e_k^j(\mathbf{q})$ represents the phonon eigenvector with wavevector \mathbf{q} of atom k in mode j, thus the scalar product $\mathbf{e}_k^j(\mathbf{q}) \cdot \mathbf{Q}$ imposes selection rules for detecting phonons. It is important to remind that \mathbf{Q} represents the total momentum transfer, and a proper choice of the Brillouin zone is fundamental. The previous scalar product underlines that only phonons with a component of polarization parallel to the scattering vector contribute to the scattering intensity. The second term of Equation 2.1.12 is known as thermal factor

$$F(E, T, \mathbf{Q}, j) = \frac{\left\langle n \left(E_j(\mathbf{Q}), T \right) + \frac{1}{2} \pm \frac{1}{2} \right\rangle}{E_j(\mathbf{Q})} \delta \left(E \mp E_j(\mathbf{Q}) \right) , \qquad (2.1.14)$$

which specifies the probability of creation or annihilation of a phonon. In Equation 2.1.14 the upper sign holds for energy loss and the lower one for energy gain by the X-rays, and the term $\langle n(E, T) \rangle$ is the thermal occupation (or Bose) factor

$$\langle n(E, T) \rangle = \frac{1}{e^{\frac{E}{k_B T}} - 1}$$
 (2.1.15)

One last important aspect concerns the scattering intensity. The flux of scattered photons into the solid angle $\Delta\Omega$ and energy interval ΔE can be written as

$$N = N_0 \frac{d^2 \sigma}{d\Omega dE} \triangle \Omega \triangle E \, n \, L \, e^{-\mu L}, \qquad (2.1.16)$$

where N_0 is the incident photon flux, n is the number of scattering units per unit volume, L is the sample thickness and μ the total absorption coefficient. The maximum IXS signal is obtained for $L = \frac{1}{\mu}$. The main responsible for intensity attenuation is the photoelectric absorption process, for energies above 10 keV. It is roughly proportional to Z⁴ (becoming quite relevant for Z > 3), far away from the electron absorption edges. Since, for small scattering vectors Q, the cross-section for Thomson scattering is more or less proportional to Z², N results to be proportional to $\frac{1}{Z^2}$. Thus, thanks to these approximation, an estimate for the inelastic X-ray scattering intensity is provided by Sinn [8]

$$I \propto \frac{L e^{-\mu L} \rho Z^2}{\Theta_D^2 M^2},$$
 (2.1.17)

where Θ_D and ρ are the Debye temperature and density, respectively.

2.2 Thermal Diffuse Scattering

Thermal motion of the atoms in a crystal gives rise to a reduction in the intensities of the Bragg reflections, and to a diffuse distribution of non-Bragg scattering in the rest of the reciprocal space. This distribution is known as thermal diffuse scattering (TDS) [9]. Thus, X-ray TDS can be exploited to study the lattice dynamics of crystals. It is an indirect method, since diffuse scattering measurements only provide information about the phonon intensities, and a detailed model for calculations is needed to extract dispersion relations. Even so, this technique can be quite valuable if combined together with inelastic X-ray scattering results, as it will be shown later in this work. The connection between this experimental technique and lattice vibrations was established around 1940, and a few years later the TDS results were used as a means to reconstruct the dispersion relations for the first time. Because of the very small TDS cross-section and the relatively low flux produced by X-ray tubes, such experiments resulted to be quite challenging from a technologically point of view, being characterized by a very slow data acquisition rate. Therefore, in the 1950's these measurements were limited to high symmetry directions. Thanks to the third generation synchrotrons, providing highly collimated beams with outstanding brilliance, and to modern two-dimensional X-ray detectors (such as image plate and CCD), allowing parallel measurements over a large solid angle, thermal diffuse scattering measurements are now feasible with high precision and efficiency. Moreover, the exceptional computational power now available enables the use of very effective and sophisticated models. With respect to the direct measurements of phonon dispersion by inelastic X-ray or neutron scattering, TDS has the advantages of a high data acquisition rate and a simple experimental setup.

2.2.1 TDS Geometry

As it can be seen in Figure 2.2.1(a), the geometry of a diffuse X-ray scattering experiment is practically identical to a X-ray diffraction experiment. The monochromatic X-ray beam is scattered from the sample in transmission geometry, and the scattered intensity distribution is recorded by an area detector. The primary beam is absorbed by a beam stop, and because of the relatively weak signal, reduction of the background can help improving the quality of the collected data, for example using a collimator in front of the sample. The incoming X-rays possess a wavevector \mathbf{k}_i , with modulus $|\mathbf{k}_i| = \frac{2\pi}{\lambda_i}$, and they are scattered by the sample and diffracted onto the Ewald sphere, which represents the accessible section of reciprocal space for a given crystal orientation. The incident beam hits the origin (0 0 0) of the reciprocal space, that is represented by a red dot in Figure 2.2.1(a). Thinking about a conventional elastic scattering process, all Bragg reflections with positions on the Ewald sphere with radius $\frac{2\pi}{\lambda_i}$ become visible. Since the monochromaticity of the incident beam is not perfect, the energy uncertainty ΔE results in a thickness $\Delta \mathbf{k}$ of the Ewald sphere (as highlighted in Figure 2.2.1(b)), and their connection is given by $\frac{\Delta E}{E} = \frac{\Delta \mathbf{k}}{\mathbf{k}}$. As displayed in Figure 2.2.1(b), it is possible to fill up a large volume in reciprocal space by rotating the sample around an axis perpendicular to the incoming X-rays and collecting the data in small angular steps.

2.2.2 Scattering Intensity

Here, a detailed description of the scattering intensity valid for both TDS and IXS is presented. The following formalism (summarized by Xu and Chiang [9]) is developed within the adiabatic approximation regime, and letting the incident beam change only the ion part of the total wave function of the system. The starting point are the results from Chapter 1, where the dynamical **D** matrix together with its eigenvalues and eigenvectors have been introduced. Just to refresh, we are considering a crystal with N unit cells, each with n atoms. The vector $\mathbf{r}_{m,s} = \mathbf{R}_m + \tau_s + \mathbf{u}_{m,s}$ gives the position of the s-th atom in the m-th unit cell, where \mathbf{R}_m is a lattice vector, and τ_s is a atomic basis vector within a unit cell. Finally, $\mathbf{u}_{m,s}$ is the displacement of the atom from its equilibrium position. Now, the time-averaged intensity of the scattered wave by the crystal, at scattering vector \mathbf{Q} is

$$I(\mathbf{Q}) = I_e \sum_{m,m',s,s'} f_s f_{s'} e^{-i\mathbf{Q} \cdot (\mathbf{R}_{m,m'} + \boldsymbol{\tau}_{s,s'})} \left\langle e^{i\mathbf{Q} \cdot (\mathbf{u}_{m,s} - \mathbf{u}_{m',s'})} \right\rangle,$$
(2.2.1)

where f_s is the atomic scattering factor (previously introduced in section 2.1.2), the $\langle ... \rangle$ denotes averaging over time and the general vector notation $\mathbf{v}_{n,n'}$ stands for $\mathbf{v}_{n'} - \mathbf{v}_n$. The term I_e is the intensity of scattering from a single electron, and it is given by



Figure 2.2.1: (a)Sketch of the diffraction geometry for a diffuse scattering experiment. (b) Large reciprocal space volume obtained from the rotation of the crystal around an axis perpendicular to the incident beam [10].

the Thomson scattering formula for a linearly polarized incident beam

$$I_e = I_{inc} \frac{e^4}{m_e^2 c^4 d^2} \left[sin^2(\phi) + cos^2(\phi) cos^2(2\theta) \right],$$
(2.2.2)

where I_{inc} is the intensity of the incoming beam, d is the distance from the scattering center to the detector, m_e is the electron mass, ϕ is the azimuthal angle between the plane of polarization of the incident beam and the scattering plane and 2θ is the scattering angle. Thanks to the harmonic approximation, it is possible to simplify Equation 2.2.1, introducing the following equivalence

$$\langle e^{i\mathbf{Q}\cdot\mathbf{u}}\rangle = e^{-\frac{1}{2}\langle(\mathbf{Q}\cdot\mathbf{u})^2\rangle},$$
 (2.2.3)

which leads to

$$I(\mathbf{Q}) = I_e \sum_{m,m',s,s'} f_s f_{s'} e^{-i\mathbf{Q} \cdot (\mathbf{R}_{m,m'} + \boldsymbol{\tau}_{s,s'})} e^{-\frac{1}{2} \left\langle \left[\mathbf{Q} \cdot (\mathbf{u}_{m,s} - \mathbf{u}_{m',s'})\right]^2 \right\rangle}.$$
 (2.2.4)

In order to proceed, it is helpful to refresh the expression for the atomic displacement $\mathbf{u}_{m,s}$, that is given by the superposition of all lattice vibration modes

$$\mathbf{u}_{m,s} = Re\left\{\frac{1}{\sqrt{\mu_s}}\sum_{\mathbf{k},j}a_{\mathbf{k},j}\mathbf{e}_{\mathbf{k},j}e^{i\left[\mathbf{k}\cdot(\mathbf{R}_m+\boldsymbol{\tau}_s)-\omega_{\mathbf{k},j}t+\varphi_{\mathbf{k},j}\right]}\right\},\tag{2.2.5}$$

where μ_s is the mass of the *s*-th atom, **k** is the wavevector, *j* represents a single vibrational mode, $\omega_{\mathbf{k},j}$ is the frequency of vibration, $a_{\mathbf{k},j}$ is the vibration amplitude and $\mathbf{e}_{\mathbf{k},j}$ the polarization vector. The phases $\varphi_{\mathbf{k},j}$ can be considered as independent variables for different modes, and this assumption brings their time average to zero. Now, using Equations 2.2.4 and 2.2.5 together with the last simplification, we get

$$\frac{1}{2} \left\langle \left[\mathbf{Q} \cdot (\mathbf{u}_{m,s} - \mathbf{u}_{m',s'}) \right]^2 \right\rangle = W_s + W_{s'} - \sum_{\mathbf{k},j} \left\{ \frac{|a_{\mathbf{k},j}|^2}{2\sqrt{\mu_s \mu_{s'}}} \right. \tag{2.2.6}$$

$$\times \left(\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s} \right)^* \left(\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s'} \right) e^{i\mathbf{k} \cdot (\mathbf{R}_{m,m'} + \boldsymbol{\tau}_{s,s'})} \right\},$$

where W_s is the Debye-Waller factor, previously introduced talking about the dynamical structure factor, and it is defined as

$$W_{s} = \frac{1}{4\mu_{s}} \sum_{\mathbf{k},j} |a_{\mathbf{k},j}|^{2} |\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s}|^{2}.$$
 (2.2.7)

Thanks to two different ways to express the energy of the system, it is possible to evaluate the amplitude of vibrations. According to a classical description, the mean kinetic energy of the system is

$$\langle E_K \rangle = \frac{N}{4} \sum_{\mathbf{k},j} |a_{\mathbf{k},j}|^2 \,\omega_{\mathbf{k},j}^2 \,. \tag{2.2.8}$$

Whereas, following the quantum theory of harmonic oscillator, the mean total energy is given by

$$\langle E \rangle = 2 \langle E_K \rangle = \sum_{\mathbf{k},j} \hbar \omega_{\mathbf{k},j} \left(\frac{1}{e^{\frac{\hbar \omega_{\mathbf{k},j}}{k_B T}} - 1} + \frac{1}{2} \right).$$
(2.2.9)

Combining Equations 2.2.8 and 2.2.9 it is possible to get this expression for the amplitude

$$|a_{\mathbf{k},j}|^2 = \frac{\hbar}{N\omega_{\mathbf{k},j}} \coth\left(\frac{\hbar\omega_{\mathbf{k},j}}{2k_BT}\right), \qquad (2.2.10)$$

and using it together with Equation 2.2.6, allows to obtain a new formula for the scattering intensity

$$I(\mathbf{Q}) = NI_e \sum_{m,s,s'} f_s f_{s'} e^{-W_s - W_{s'}} e^{-i\mathbf{Q} \cdot (\mathbf{R}_m + \boldsymbol{\tau}_{s,s'})} e^{G_{m,s,s'}(\mathbf{Q})},$$
(2.2.11)

where the term G of the last exponential is

$$G_{m,s,s'}(\mathbf{Q}) = \frac{\hbar}{2N\sqrt{\mu_s\mu_{s'}}} \sum_{\mathbf{k},j} \left[\frac{1}{\omega_{\mathbf{k},j}}\right] (\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s})^* \left(\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s'}\right) \\ \times \coth\left(\frac{\hbar\omega_{\mathbf{k},j}}{2k_BT}\right) e^{i\mathbf{k}\cdot(\mathbf{R}_m + \boldsymbol{\tau}_{s,s'})}.$$
(2.2.12)

In Equation 2.2.11, the summation over m' has been replaced by N, only leaving the summation over m, thanks to the translational invariance of the crystal. Thus, it represents the general formula for the evaluation of IXS and TDS intensity, but it results to be too computationally demanding because of the two nested three-dimensional

summation, both in real and reciprocal space. One more simplification can be introduced by treating the term G as a small quantity, and proceeding with a Taylor expansion of the exponential $e^x = 1 + x + \frac{x^2}{2} + \ldots$, which allows to obtain

$$I(\mathbf{Q}) = I_0 + I_1 + I_2 + \dots$$
 (2.2.13)

Here the first term, I_0 , corresponds to Bragg diffraction, where the Debye-Waller factor accounts for the intensity reduction due to the temperature influence. Using the identity

$$\sum_{m} e^{i\mathbf{k}\cdot\mathbf{R}_{m}} = N \sum_{l} \delta(\mathbf{Q} - \mathbf{K}_{l})$$

where \mathbf{K}_l denotes the reciprocal lattice vectors, it is possible to write the first-order term I_1 as

$$I_{1} = \frac{\hbar N I_{e}}{2} \sum_{j} \left\{ \left[\frac{1}{\omega_{\mathbf{k},j}} \coth\left(\frac{\hbar \omega_{\mathbf{k},j}}{2k_{B}T}\right) \right]_{\mathbf{k}=\mathbf{Q}-\mathbf{K}_{\mathbf{Q}}} \right.$$

$$\times \left| \sum_{s} \frac{f_{s}}{\sqrt{\mu_{s}}} e^{-W_{s}} (\mathbf{Q} \cdot \mathbf{e}_{\mathbf{k},j,s}) e^{-i\mathbf{K}_{\mathbf{Q}} \cdot \boldsymbol{\tau}_{s}} \right|_{\mathbf{k}=\mathbf{Q}-\mathbf{K}_{\mathbf{Q}}}^{2} \right\}.$$

$$(2.2.14)$$

The vector $\mathbf{K}_{\mathbf{Q}}$ is the nearest reciprocal lattice vector to \mathbf{Q} , and $\mathbf{k} = \mathbf{Q} - \mathbf{K}_{\mathbf{Q}}$ is the reduced wavevector of \mathbf{Q} in the first Brillouin zone. Now it is useful to exploit the following relation

$$\mathbf{e}_{\mathbf{k}+\mathbf{K},j,s} = \mathbf{e}_{\mathbf{k},j,s} e^{-i\mathbf{K}\cdot\boldsymbol{\tau}_s},\tag{2.2.15}$$

which represents the fact that the polarization vectors are not periodic in reciprocal space within the dynamical \mathbf{D} matrix formalism. It allows to introduce the onephonon structure factor as

$$F_j(\mathbf{Q}) = \sum_s \frac{f_s}{\sqrt{\mu_s}} e^{-W_s} (\mathbf{Q} \cdot \mathbf{e}_{\mathbf{Q},j,s}).$$
(2.2.16)

Thus, the final result for the first-order term for the scattering intensity is

$$I_1 = \frac{\hbar N I_e}{2} \sum_j \left[\frac{1}{\omega_{\mathbf{Q},j}} \coth\left(\frac{\hbar \omega_{\mathbf{Q},j}}{2k_B T}\right) |F_j(\mathbf{Q})|^2 \right].$$
(2.2.17)

It describes the process of single phonon scattering, which is often the dominant contribution, particularly at modest or low temperatures. An important property of the
first-order scattering intensity is that at a given scattering vector \mathbf{Q} , it involves one phonon of any of the 3n branches at the same wavevector, because of momentum conservation. The total TDS is given by the sum of the scattering produced by all branches. Equation 2.2.17 does not involve nested three-dimensional summation any more, therefore being easy for numerical evaluation. Here a strong influence by the thermal population factor is present inside the *coth* function, thus the low energy phonons (in particular the acoustic phonons close to Bragg peaks) contribute the most to the diffuse scattering signal.

Chapter 3

Experimental Facility

The main experiments that will be described in this thesis were conducted at ID28 beam line of European Synchrotron Radiation Facility (ESRF) in Grenoble. ID28 is the inelastic X-ray scattering beam line dedicated to the study of lattice dynamics in condensed matter. Currently ID28 is not equipped for TDS measurements, therefore the ID23 beam line was used for the diffuse scattering measurements. ID23 is the highly automatized macromolecular crystallography beam line. Before proceeding with the description of the beam lines instrumentation, a brief description of synchrotron radiation is introduced.

3.1 Synchrotron Radiation

Charged particles moving at relativistic speed, which are forced to follow curved trajectory by magnetic fields, emit electromagnetic radiation in the direction of their motion, which is known as synchrotron radiation (for more details, see [11]). It was observed for the first time in 1947 at the General Electric synchrotron in the USA, but it was only at the end of the 1960's that it was realized its usefulness for condensed matter research. In our case of interest (ESRF), the charged particles are electrons; they are generated by an electron gun, and the first step consists in accelerating the electron in a linear accelerator, or 'linac', where they reach an energy of about 200 MeV. As the electrons reach the desired energy, they are injected in the booster stage, which is a 300 m circular accelerator in which electrons get to their final energy of 6 GeV. The final step is the injection inside the storage ring, where electrons follow a many sided polygon path under the action of magnets placed along the circumfer-



Figure 3.1.1: Schematic view of a synchrotron radiation facility [11].

ence (bending magnets). Figure 3.1.1 shows a schematic representation of the above described facility. Of course, once in the storage ring, electrons lose some of their energy during the process of light emission: thus, the storage ring is equipped with radio frequency cavities, which allow to restore the energy of electrons after an energy loss event. While it is possible to obtain X-ray radiation from a bending magnet, a much more efficient way is through the use of insertion devices. Here the insertion devices are placed on straight sections of the storage ring, between the bending magnets. They consist of a periodic of magnets which produce an alternating magnetic field, and inducing the electrons to oscillate perpendicularly to their direction of motion in the horizontal plane, allowing the electron to emit X-rays as it changes velocity. A specific type of insertion device, known as an undulator, is designed so that the oscillations of a single electron will be in phase, hence producing a cone of emitted radiation that is orders of magnitude more intense, and much narrower than the one produced by a bending magnet. Moreover, the undulators can be easily tuned changing the gap between the magnets.

The synchrotron radiation produced by undulators, possesses the following peculiar properties:

• narrow spectral range, that can be adjusted by changing gap and periodicity of the magnets;

- high photon flux, which is fundamental for phonon experiments, because of low counting rates;
- pulsed time structure (general for synchrotron light);
- high brilliance, allowing to obtain spot size on the target of the order of a few μm , so that very small sample can be investigated with outstanding spatial resolution;
- high level of linear (horizontal) polarization can be achieved.

3.2 Beam Line ID28

Beam line ID28 is dedicated to the study of phonon dispersion in condensed matter at total momentum transfers, \mathbf{Q} , and energy transfers, E, characteristic of collective atom motions. It operates in the hard X-rays regime, in fact choosing the appropriate geometry for the monochromator it is possible to obtain six different incident energies of 13840, 15817, 17794, 21747, 23725 and 25704 eV. The scientific cases which can be studied in ID28 are divided into three groups:

- 1. determination of phonon dispersions in crystalline materials;
- 2. study of the high-frequency collective dynamics in disordered systems (such as quantum liquids, glass formers and biological materials);
- 3. determination of dispersion relations under extreme conditions: pressure up to 100 GPa and temperature of 1000 K can be achieved.

Thanks to phonon dispersions it is possible to access various material properties, like elastic constants, phonon-phonon interaction, electron-phonon coupling and dynamical instabilities.

The instrumentation of ID28 is based on the triple-axis spectrometer, previously developed by Brockhouse for inelastic neutron scattering. As it can be noticed in Figure 3.2.1, in the first axis the energy of the incident X-rays from the undulators is selected. Afterwards, the monochromatic beam hits the sample, whose position, orientation and scattering angle are selected, this is the second axis. After choosing the scattering angle, the third and last axis is the crystal analyzer, which specifies the scattered photon energy to be detected. Of course, this three-steps description is just a simplified version of the real and entire path of the beam. Before reaching



Figure 3.2.1: Beam line ID28 schematic layout.

the main monochromator, the X-rays (initial bandwidth $\frac{\triangle E}{E} \approx 10^{-2}$) undergo a premonochromator stage. It is composed by a pre- and a post-monochromator, which improve the energy resolution to $\frac{\Delta E}{E} \approx 10^{-4}$ and $\frac{\Delta E}{E} \approx 10^{-5}$, and they consist of Si(111) and Si(400) channel-cut single crystals (kept in high vacuum), respectively. The main goal of this stage is to reduce the heat load on the main monochromator, thus preventing thermal expansion and damages on the main-crystal monochromator. Then the beam reaches the backscattering monochromator, that is a Si(h h h) crystal, with h = 7, 8, 9, 11, 12 and 13, each corresponding to the energy values previously listed, respectively: it finally provides the wanted energy resolution of $\frac{\Delta E}{E} \approx 10^{-7} - 10^{-8}$. Now the highly monochromatic beam needs to be properly focused onto the sample, and this can be achieved in different ways. Both horizontal and vertical focusing can be obtained using the platinum-coated toroidal mirror, placed just after the main monochromator, at 25 m from the target. This configuration allows to obtain a beam size of $500 \times 80 \,\mu m^2$ (on the sample) in the horizontal and vertical direction, respectively. For a smaller focal spot, the toroidal shape of the mirror is switched to cylindrical one. To improve the horizontal focusing, the cylindrical mirror configuration is used in conjunction with a platinum-coated mirror at 2.5 m from the sample. With this configuration the beam is focused to a size of $25 \times 80 \, \mu m$. After hitting the sample the sample, the energy of the scattered photons are analyzed by the spherical silicon crystal analyzers at the end of the 7 m spectrometer arm. ID28 is equipped with 9 analyzers, which are arranged in the horizontal plane with a fixed angular offset. These silicon crystals Bragg-reflect the beam onto 9 corresponding detectors: this is quite challenging, since the analyzers must be built in such a way that the Bragg angles are identical for all the incident photons. It can be realized using crystals with a spherical surface whose radius equals the sample-analyzer distance. This is known as Rowland condition, and it is schematically displayed in Figure 3.2.2. Of course, it is not possible to get a high quality crystal with such a shape, without deformations and high level of stress. Thus, it consists of a spherical substrate on which approximately 12000 perfect silicon crystals ($0.6 \times 0.6 mm^2$ surface size, and 3 mm thick) are attached. Finally, the analyzed photons reach the silicon diode detector with an active area of $3 \times 8mm^2$; the detector has a very low dark noise level of about 1 count in 30 minutes. Before proceeding, it is important to underline a very important thing. The analyzers are mounted on a 7 meters arm, which can be rotated between 0 and 45° around a vertical axis passing through the sample position. Moving this arm corresponds to a motion of the scattering angle 2θ , and it allows to choose the momentum transfer



Figure 3.2.2: Sketch of the Rowland condition for crystal analyzers.

during an experiment.

3.2.1 High Energy Resolution

As discussed in Chapter 2, the scattering geometry defines the momentum and energy transfer resulting from the scattering process at the sample. Now, in order to perform an IXS experiment, we are interested in measuring the energy transfer at constant scattering angle, thus keeping fixed the 2θ angle. It is achieved by changing the lattice parameter of the analyzer or the main monochromator, that means changing the temperature of the crystals. Since there are nine crystal analyzers, it is much more reliable to act on the temperature of the monochromator (only one crystal), where the relationship between energy and lattice parameter is $\frac{\Delta E}{E} = \frac{\Delta d}{d} = \alpha \Delta T$, with $\alpha = 2.58 \times 10^{-6} K^{-1}$ the thermal expansion coefficient of silicon at room temperature. This means that in order to obtain an energy step of about one tenth of the energy resolution, we need to control the monochromator temperature with a precision of about $0.5 \, mK$. A high-order Bragg reflection and a perfect crystal are mandatory to obtain the desired energy resolution. The resolving power is connected to the order of Bragg

reflection by $\frac{\Delta E}{E} = \frac{d_{hkl}}{\pi \Lambda_{ext}}$, where d_{hkl} is the lattice spacing associated with the (hkl) reflection order, and Λ_{ext} denotes the primary extinction length (from the dynamical theory of X-ray diffraction, [7]). The quantity Λ_{ext} increases with increasing reflection order, which has to be high enough to achieve the required energy resolution. The other fundamental ingredients to reach the very low value of ΔE , is the backscattering configuration. The relation of energy to wavevector for X-rays leads to a simple expression for the energy resolution

$$\frac{\delta E}{E} = \frac{\delta k}{k} \,. \tag{3.2.1}$$

Now, assuming that an incoming beam with wavevector k hits the sample with a Bragg angle θ , the Bragg's law is

$$2k\sin(\theta) = \tau, \qquad (3.2.2)$$

where τ represents the length of a reciprocal lattice vector. Thus, it is possible to associate an uncertainty $\delta\theta$ to the scattering angle, which represents the angular divergence of the beam. It produces an uncertainty δk on the wavevector, that affects the energy as well. From Equation 3.2.2, it is possible to obtain

$$\left(\frac{\delta k}{k}\right)_{\theta} = \cot(\theta)\,\delta\theta\,,\tag{3.2.3}$$

that represents the contribution of the scattering geometry on the energy resolution [6]. From Equation 3.2.3, it is possible to notice that this contribution can be minimized using a scattering angle close to 90°: this is the reason to operate close to the backscattering geometry.

3.3 Beam Line ID23

The beam line is composed of two independent end-stations which operate concurrently. We are interested in ID23-1, a macromolecular crystallography beam line, that has a tunable energy in the range of 5 - 20 keV. It is a highly automatized beam line, in fact it allows remote semi-automatic sample alignment, and thanks to an automated sample changer the users can also run their experiment even not being physically present at ESRF. The main applications of this laboratory, it the intense study of fundamental protein structures. As previously mentioned, thermal diffuse scattering measurements share the same experimental configuration of a diffraction measurement, thus allowing to exploit the ID23-1 experimental setup for TDS. A sketch of



Figure 3.3.1: Beam line ID23-1 schematic layout. (a) Optic hutch and (b) experiment hutch.

ID23-1 is displayed in Figure 3.3.1. The white beam coming from the undulators gets attenuated before hitting the monochromator, which is a silicon (1 1 1) channel-cut crystal: it is kept under high vacuum and cooled by liquid nitrogen. Of course the monochromator is fully motorized in order to rotate it and change the energy of the resulting monochromatic beam. The slits are placed just after the monochromator define size and position of the monchromatic beam, and they also reduce the background coming from the white beam. The other fundamental component of the optic hutch is the rhodium-coated toroidal mirror; thanks to it the beam is properly focused. Inside the experimental hutch, a cryostream device is always present very close to the sample holder, and it allows to control the sample temperature with very high accuracy, and to keep it steady during the measurements. The fluorescence detector is mainly used to center the beam. Thanks to the very user-friendly interface this procedure is

very fast, as it is the procedure to find the center of rotation of the sample. In order to reduce the air scattering, improving the quality of the acquired signal, a collimator in front of the sample (not always used) and a beam stop just behind the sample are exploited. The X-rays diffracted from the target are finally detected from the area detector, that in this case is a PILATUS detector, based on the silicon hybrid pixel detector system [12]. It currently represents the best option available for TDS studies with X-ray energies up to 20 keV. This detector operates in single photon counting mode and has practically zero dark current and zero read-put noise. The active area is $423.6 \times 434.6 \, mm^2$, the pixel size is $172 \times 172 \, \mu m^2$ for a total of 2463×2527 pixels. Finally, the read-out time is $3 \, ms$ and the frame rate is $25 \, Hz$. All these properties characterize a very powerful detector, which allows to obtain extremely high quality data.

Chapter 4

Vanadium Dioxide

4.1 Introduction

Vanadium dioxide has been widely studied along the past decades, mainly thanks to its spectacular metal-insulator transition. It is neither the only vanadium oxide compound, nor the only transition metal oxide to show such an interesting behaviour, we can think about V_2O_5 , V_2O_3 , NbO₂, and many others [13, 14, 15, 16], but VO₂ is attracting much more attention with respect to the others because of its transition temperature ($T_{MIT} \approx 340$ K), which is relatively close to the room temperature. From the scientific point of view, metal-insulator transition (MIT) is a topic of long-standing interest in condensed matter physics. Experimental and theoretical studies of the MIT phenomenon in VO₂ have been active for more than half a century. Despite this large amount of research, the mechanism responsible for the metal-insulator transition in VO₂ has yet to be clearly identified. In addition to being interesting from a fundamental viewpoint, vanadium dioxide has recently drawn a lot of enthusiasm thanks to the wide range of possible technological applications for which it can be exploited.

4.1.1 Properties

This impressive MIT process is also accompanied by a structural phase transition (SPT), where a high temperature metallic tetragonal lattice (rutile structure) transforms to a low temperature insulating monoclinic one. Anyway, the VO₂ crystal structure topic deserves a more detailed discussion, which will be provided later in this chapter; now I am going to focus on the charming properties of this material, which

are possibly linked to different technological applications. Of course, the first one that needs to be underlined, is the 4 to 5 order abrupt decreasing (depending on the sample as described by Ruzmetov & Ramanathan [17]) of the resistance across the transition, as it has been highlighted in the work done by Mun *et al.* [18], and shown in Figure 4.1.1.



Figure 4.1.1: Resistance as a function of the temperature across the metal-insulator transition [18].

These results were accomplished by studying a single crystal VO_2 sample, but it is possible to obtain slightly different values for the transition temperature, the resistance variations and the hysteresis width, depending on:

- the kind of sample we are talking about, for example if it is a single crystal needle, or a thin film;
- the experimental technique utilized for the sample growth.

Another feature of VO_2 is that the MIT can be tuned through external applications: for example, the proper choice of the substrate for a thin film growth, can induce a compressive (or tensile) strain along the rutile c-axis which produces a decrease (or increase) in the transition temperature, allowing to bring it as low as 300K as pointed out by Muraoka and Hiroi [19]. Furthermore, there is also another way to change the properties of vanadium dioxide, which exploits the role of substituents like tungsten and titanium in order to tune both the T_{MIT} and the hysteresis width.

Of course, electrical properties are not the only ones which undergoes a drastic variation across the transition as discussed by Soltani *et al.*: a study of the infrared transmittance in the heating cycle (see Figure 4.1.2) reveals that VO_2 optical characteristics are changing too [20].



Figure 4.1.2: Infrared transmittance as a function of the temperature across the transition, for VO_2 on quartz substrate [20].

In order to introduce the next section, it is useful to spend a few words about one last quality about the MIT: the metal to insulator transformation (and vice versa) is an ultrafast process that makes this material an extremely powerful tool. Indeed, the phase transition can be triggered at subpicosecond timescales, as it is resumed by Yang *et al.*, who collected the results obtained by different experimental techniques [16].

4.1.2 Technological Applications

Before proceeding, it does worth to talk about a couple of examples concerning real world enforcement of vanadium dioxide. From all the characteristics briefly introduced above, it is straightforward to notice that we are talking about a material that has a lot of intriguing qualities. Indeed, VO₂ has being studied during these years for a very different set of technological applications, thus it can be quite interesting to give a short panoramic about them. Of course, a central theme in devices exploring metal-insulator transition is the realization of an ultrafast switch: combining the significant change in resistance with the superfast transformation which lasts only few hundreds of femtoseconds, makes VO₂ a perfect candidate for this kind of devices. The only problem is the MIT triggering mechanism, since a temperature change does not match very well with electronic switch devices: this obstacle was solved by Stefanovich *et al.*, who reported that an electric field or electron injection in VO₂ can trigger the metal-insulator transition (E-MIT), opening the path for a new family of field effect transistors (see Figure 4.1.3(a) for a schematic representation of the apparatus) [21].



Figure 4.1.3: Two examples of devices. (a) Schematics of a VO₂ electronic switch device [16]. (b) Electro-optical switch device, for $\lambda = 1.55 \, \mu m$ [20].

Of course, it is possible to think about some other kind of application, exploiting the optical properties of vanadium dioxide. An example is shown in Figure 4.1.3(b) from the work of Soltani *et al.*, whose group built an electro-optical switch apparatus, utilizing the E-MIT as above mentioned. Instead, without the help of any electrical triggering mechanism, it is possible to get a thermochromic coating which is based only on the natural characteristics of this material, and results to be attractive as a

passive smart radiator device for spacecrafts [20].

4.2 VO₂ Structure

As previously noted, the metal-insulator transition is accompanied by a structural phase transition, but the situation is much more complicated than it has been introduced before. Two different monoclinic phases, known as M1 and M2, can be recognized, moreover a third insulating triclinic T phase also exists, while in the metallic phase the only structure is the rutile R (tetragonal) one. Here I will mainly focus on the most important ones, which are M1, M2 and obviously the rutile.

4.2.1 Rutile Phase

The rutile phase appears above approximately 340 K, depending on the quality and the kind of sample as already remarked. The vanadium dioxide metallic structure is simply based on a traditional tetragonal lattice, with space group $P4_2/mnm$. The Wyckoff positions of the atoms within the unit cell displayed in Figure 4.2.1 are [22]:

- (2a): (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for the metal atoms;
- (4f): $\pm(u, u, 0)$ and $\pm(\frac{1}{2} + u, \frac{1}{2} u, \frac{1}{2})$ for the oxygen atoms.

According to McWhan et al. [23], the lattice constants are

$$a_R = 4.5546 \,\text{\AA},$$

 $c_R = 2.8514 \,\text{\AA}$

and the internal oxygen parameter is u = 0.3001. From Figure 4.2.1 it is rather easy to visualize the rutile structure as a body centered tetragonal pattern formed by the metal atoms, each of them surrounded by an oxygen octahedron. Octahedra centered at the corners and the center of the cell are rotated by 90° about the tetragonal *c*-axis relative to each other, and because of this feature the lattice translational symmetry reduces to simple tetragonal. It is interesting to put the attention on the VO₂ tetragonal *c*-axis: comparing its length with neighboring rutile systems, it emerges that it is slightly shorter than the other ones, and this behaviour can be linked to the insulating structure, as we will see. A possible explanation is given by Goodenough [24], who suggested the *d* electrons to be responsible for this short distance, since



Figure 4.2.1: The tetragonal metallic structure. The big, red spheres represents the metal atoms, while the small blue ones are the oxygen atoms. It is possible to notice the oxygen octahedron which surrounds each vanadium [22].

they are able to provide additional binding either through direct overlap of d orbitals of adjacent vanadium atoms, or thanks to the oxygen atoms on the shared edge of contiguous oxygen octahedra. It is useful to spend a few words about the vanadium d orbitals, which are shown in Figure 4.2.2. This choice of Cartesian axes is consistent with the choice displayed in Figure 4.2.1, where it is possible to notice that there exist two differently oriented octahedra: because of the orientation, it is possible to define two distinct z axes. Here, in contrast to the traditional orientation of the x and y axes towards the metal-ligand bonds, the coordinate systems have been rotated by 45° about the local z axis such that they are parallel and perpendicular, respectively, to the rutile c axis. Now we focus on the octahedra at the center of the tetragonal cell. The angular parts of the d orbitals which are exhibited in Figure 4.2.2(a) and (b) represent the e_g states, resulting from the octahedral crystal field splitting of the metal d orbitals. Instead, the t_{2g} states are built from the orbitals from Figure 4.2.2(c), (d)



Figure 4.2.2: Angular parts of the *d* orbitals. (a) $d_{3z^2-r^2}$, (b) d_{xy} , (c) $d_{x^2-y^2}$, (d) d_{xz} and (e) d_{yz} [22].

and (e). Starting from these last three pictures, it is possible to observe the following remarks:

- the $d_{x^2-y^2}$ orbitals point along the c_R and the local y axes, thus these orbitals provide a σ -type overlap between metal sites along the vertical chains formed by the octahedra;
- the d_{yz} states point forward the $\langle 100 \rangle$ directions. As a consequence, they mediate π -type overlap between metal atoms on the vertical chains;
- the d_{xz} give a small σ -type overlap with their counterparts at metal sites translated by the vectors $\langle 1, 0, 0 \rangle$.

These statements are due to the particular choice of coordinate system; as follow the overlap of both the $d_{x^2-y^2}$ and d_{yz} orbitals with orbitals of the same type at neighbouring sites connects atoms, which are separated by vectors of the simple tetragonal lattice. On the other hand, coupling between atoms, which are located at the corner and in the center of the cell, is provided by the d_{xz} parts.

4.2.2 M1 Phase

At standard condition of pressure and below approximately 340 K, the vanadium dioxide shows the well known M1 phase. The first significant experimental results about this structure, had been provided by Andersson in 1956; indeed, before this year, the room temperature phase of VO₂ was thought to be a simple tetragonal one. Thanks to his work, Andersson proved that assertion to be wrong, since the M1 phase is a simple monoclinic structure (as displayed in Figure 4.2.3), with space group $P2_1/c$ [25].



Figure 4.2.3: M1 structure of vanadium dioxide. Distinction between two types of oxygen atoms is underlined [22].

A structural refinement study of VO_2 was done by Longo and Kierkegaard, and it has led to the following values for the lattice parameters [26]

$$a_{M1} = 5.7517 \,\mathrm{A},$$

 $b_{M1} = 4.5378 \,\mathrm{\AA},$
 $c_{M1} = 5.3825 \,\mathrm{\AA},$
 $\beta_{M1} = 122.646^{\circ}.$

The general Wyckoff positions (4e) of both the vanadium and oxygen atoms are $\pm(x, y, z)$ and $\pm(x, \frac{1}{2} - y, \frac{1}{2} + z)$, and the atomic positions determined by Longo & Kierkegaard (in agreement with the results by Andersson) are listed in Table 4.2.1. Now, a comparison between the phases examined so far, can bring to some interesting observations. The monoclinic phase can be seen as a distortion of the high-temperature tetragonal one. Indeed, inspecting the two different structures of Figure 4.2.1 and Figure 4.2.3

Atomic	Wyckoff positions		Parameters	
		x	У	z
V	(4e)	0.23947	0.97894	0.02646
\mathbf{O}_1	(4e)	0.10616	0.21185	0.20859
O_2	(4e)	0.40051	0.70258	0.29884

Table 4.2.1: Atomic positions of the monoclinic M1 structure of VO₂ [26].

together with the lattice constants, it is possible to find simple relations between the unit cell vectors:

$$\mathbf{a}_{M1} \approx 2 \mathbf{c}_R, \ \mathbf{b}_{M1} \approx \mathbf{a}_R, \ \mathbf{c}_{M1} \approx \mathbf{b}_R - \mathbf{c}_R,$$

resulting in a monoclinic unit cell that is twice the size of the tetragonal one [27]. Observing Figure 4.2.3 it is possible to notice a striking feature of this monoclinic phase, the metal-metal pairing along the rutile *c*-axis (dimerization process), as discussed by Goodenough [24]. This leads to two different V-V distances of 2.619 and 3.164 Å. In addition to this coupling, the vanadium atoms are also tilted with respect to the c_R direction, resulting in a zigzag-like pattern, and together these two anomalies bring to the following modifications:

- there are two different apical vanadium-oxygen bond lengths of 1.77 and 2.01 Å;
- two short and two long equatorial V-O bond lengths of 1.86, 1.89, 2.03 and 2.06 Å arise.

This quite big variety of distances is also due to the fact that the oxygen atoms forming an octahedra, do not strictly follow the vanadium shifts, and stay almost at their original position.

4.2.3 M2 Phase

This time vanadium dioxide crystallizes in a centered monoclinic lattice, with a space group C2/m. The first reliable results are from Marezio *et al.* measurements on $V_{0.976}Cr_{0.024}O_2$ (the reason of chromium substituents is explained later) in 1972, when

they got the following values for the lattice constants [27]

$$a_{M2} = 9.0664 \text{ \AA},$$

 $b_{M2} = 5.7970 \text{ \AA},$
 $c_{M2} = 4.5255 \text{ \AA},$
 $\beta_{M2} = 91.88^{\circ}.$

It is possible to notice from Figure 4.2.4 that there exist two different types of vanadium atoms and three different types of oxygen atoms within this structure. Here,



Figure 4.2.4: Monoclinic M2 phase of VO₂ [22].

because of their locations inside the unit cell, these five kind of atoms will occupy subsets of the general Wyckoff position (8j): $\pm(x, y, z), \pm(x, -y, z), (\frac{1}{2}, \frac{1}{2}0) \pm(x, y, z)$ and $(\frac{1}{2}, \frac{1}{2}0) \pm (x, -y, z)$. All the values are listed in Table 4.2.2. From Figure 4.2.4 it is possible to identify V₁ and V₂ as the metal atoms at the corners and centers, respectively, of the hidden rutile cell. For what concerns oxygen atoms, O₁ are placed at the apices of the octahedra centered about V₁ atoms, in contrast O₂ and O₃ are equatorial atoms for V₁ and apical atoms for V₂. Another couple of discriminating features of this phase can be distinguished:

• only the V₁ chains dimerize, without showing the zigzag-like pattern;

Atomic	Wyckoff positions	Parameters		
		x	У	z
\mathbf{V}_1	(4g)	0.0	0.7189	0.0
\mathbf{V}_2	(4i)	0.2312	0.0	0.5311
01	(8j)	0.1460	0.2474	0.2865
O_2	(4i)	0.3975	0.0	0.2284
03	(4i)	0.0980	0.0	0.7862

Table 4.2.2: Crystal structure parameters of the M2 phase [27].

• the other half (composed by the V₂ atoms) of the chains experiences the zigzaglike displacement, but no pairing appears.

Thus, there exist three different metal-metal distances along these chains direction, with 2.538 and 3.259 Å within the V₁ chains, and uniform spacing of 2.933 Å along the V₂ chains.

Before closing this section, it is mandatory to shortly discuss a fundamental characteristic of the M2 monoclinic phase: it does not exist without strain. Indeed, in the earlier experiments done to study this structure, Marezio *et al.* and Ghedira *et al.* had to use substituents like chromium and aluminium in order to induce internal stress, that allows to see the M2 phase at room temperature [27, 28]. A recent work by Mun *et al.* shows that it is also possible to obtain this monoclinic structure in pure VO₂ samples, because of internal strain inside the large-size single crystals [29]. Thus they discovered that a second structural phase transition occurs at about



Figure 4.2.5: (a) The IIT transition involving M1 and M2 phases is visible between 45 and 50° [6]. (b) Stress-temperature phase diagram of VO₂ [30].

320 K (heating process) accompanied by a slight increase of resistance, as shown in Figure 4.2.5(a): this is the evidence of the insulator-insulator transition from M2 to M1 phase. Another very nice experiment is discussed by Park *et al.* with the goal of studying the boundaries between the different structures [30]. Thanks to the improving in sample growth techniques, they were able to get VO₂ nanobeams allowing high level control of the metal-insulator transition: this way it was possible to obtain the phase diagram displayed in Figure 4.2.5(b).

4.3 Peierls vs Mott Mechanism

As previously introduced, the process which lies below the metal-insulator transition is still a subject of debate, although many efforts have been done to study vanadium dioxide. There are two different mechanisms which can explain the opening of the energy gap starting from the metallic phase. The first one is the so called Mott mechanism, which takes into account the role of the electron-electron interaction within the energy bands formation of a crystal. It happens, indeed, that the conventional band theory, which considers the band structure to be formed solely due to the periodic crystal structure, fails in the description of the band structure of some materials. This is the case of some transition metal oxides which show to be insulator (or better, semiconductor) materials, while the band theory predicts them to be metals. The reason for this behaviour can be addressed to the electron-electron correlation, which consists in a strong Coulomb repulsion between the electrons. Mott gave a simple picture in order to describe this phenomenon: where we expect the formation of a single band from the overlap of atomic orbitals, the presence of strong Coulomb interaction is responsible for the splitting of the single band into two different bands, so that the lower one is completely occupied and the upper is empty, resulting as an insulator system. When this is the process which leads to the metal-insulator transition, the compound is named Mott (or Mott-Hubbard) insulator.

It is not the only possible option to explain the energy gap opening of a metal. The MIT process can also originate from electron-lattice interactions, in which case the compound is referred to as Peierls insulator. A Peierls transition is due to structural changes inside the material, that is a lattice deformation. This means that the periodic structure of the compound changes, bringing to an energy band structure modification and to the opening of the gap. The first experimental evidence of the Peierls mechanism leading a metal-insulator transition was found in the 1960's, trying to follow Little's idea that some organic materials could possibly show to be superconductor at high temperature thanks to the almost one-dimensional chains conduction. Instead of revealing superconducting behaviour, such metallic materials (like TTF-TCNQ) undergo an insulating transition decreasing the temperature [31]. Thus, this kind of process results to be particularly effective on low dimensional systems: because of this, a simple model based on a one-dimensional system can help to understand how the Peierls transition works. Let's think about a one-dimensional metal with a half-filled band and in the absence of any electron-electron or electronphonon interactions, so that the situation is like it is displayed in Figure 4.3.1(a). After the electron-lattice interaction comes into play, it results to be energetically fa-



Figure 4.3.1: One-dimensional metal undistorted and with lattice parameter a (a), and after Peierls distortion (b) [32].

vorable to insert a lattice distortion with period λ , that is directly connected to the

Fermi wave vector k_F by the following relationship

$$\lambda = \frac{\pi}{k_F} \,,$$

thus, resulting in a sort of dimerization process of the atoms [32]. In this case, this process brings to a new lattice constant being the double of the initial one-dimensional chain as displayed in Figure 4.3.1(b). Of course, the decrease of the electronic energy is not the only change happening across the transition: the rearrangement of the atoms along the chain brings to an increase of the elastic energy, consequently, a condition of energy gain for the coupled electron-phonon system has to be fulfilled.

Experimental results supporting both the mechanisms have been collected, thus creating two groups of supporters within the scientific community, following either one theory or the other one. Here it can be helpful to briefly cite a couple of examples. One of the arguments used in favor of the Mott process is based on the fact that either with little quantities of chromium substitution or applying external uniaxial pressure to pure VO_2 , it is possible to obtain another two other different insulating phases:

- 1. the M2 phase, with a monoclinic structure as previously described;
- 2. T, a triclinic structure that works as intermediate phase between the two monoclinic phases.

Thus, the existence of three different vanadium dioxide structures with different characteristics and very similar electrical properties, could be seen as a proof that the lattice transformation is not the main responsible for the metal-insulator transition. Inside their paper, Zylbersztejn and Mott introduced this idea in order to support their main discussion [33]. They believe that the distortion introduced by the structural phase transition it not enough to open the energy gap of the insulating phase, and in order to explain this feature, it is needed to consider the picture in which the electrons are placed in states localized by the Hubbard U, so that the electron-electron correlation is the mechanism responsible for the gap opening.

On the other hand, Cavalleri *et al.* provided one simple proof that a Peierls mechanism is involved in the transition [34]. Thanks to ultrafast pump-probe reflectivity experiments, it was possible to study the dynamics of the reflectivity change due to the metal-insulator transition, with femtosecond resolution. The experimental results revealed that the lower limit for the transition time is 80 fs, while according to theoretical previsions it should have been much shorter if the MIT were caused by pure electronic effects. Of course, this is neither a proof that the electron-lattice interaction is the main responsible, nor it means that a Mott process is completely absent, and indeed, the situation could not be as black and white as it has been thought for many years. Now, before proceeding with some existing results about VO_2 lattice dynamics, it is very important to give a complete picture of the electronic band structure.

4.4 Band Structure

The first convincing model about vanadium dioxide energy band structure was provided by Goodenough in 1971, and it is based on a molecular orbital picture [24]. The most important atomic orbitals that have to be considered are the vanadium 3d and the oxygen 2p orbitals. Together with these orbitals, there are two features playing a central role in the band structure formation, and they are the hybridization of the two orbitals just mentioned, and the symmetries of the crystal lattice. In fact, as previously discussed the octahedral crystal field is responsible for the removing of the degeneracy of the five V 3d orbitals: in more details, the cubic component provided by the V⁴⁺-ion splits the 3d levels into two degenerate e_g states and three degenerate t_{2g} states. Now, it still remains an orthorhombic part of the crystal field, such that the degeneracies are further removed in the following final states (very small energy discrepancies from the previous step):

- the two e_g orbitals are split into two d_σ orbitals (following Goodenough notation);
- the three t_{2g} orbitals are split into two d_{π} orbitals and a $d_{||}$ orbital.

As it can be noticed in Figure 4.2.2 the two d_{σ} orbitals point towards the oxygen atoms of the octahedra surrounding a vanadium atom: because of this configuration, the two e_g orbitals are connected between themselves through the oxygen (working like ligand) 2p orbitals, forming a σ -type bond. Of course it results in the formation of a σ band thanks to the periodic structure of the crystal, and together with its antibonding counterpart (σ^*), they lie further away from the Fermi level (see Figure 4.4.1). Now, the two d_{π} orbitals are mainly responsible for the formation of the π and π^* bands, again thanks to the hybridization with the ligand 2p orbitals. For what concern the remaining $d_{||}$ orbital, it has a strong component lying along the rutile c-axis, providing a direct overlap with other orbitals of the same kind. In the metallic phase, no direct bond is present between vanadium along the c_R direction, so that the final result is the rising of a $d_{||}$ band around the Fermi level. Within the rutile structure, the π^* bands also lies around the Fermi level, but with a slightly higher energy with respect the $d_{||}$, because of the hybridization process. The final result in this situation is the presence of a $d_{||}$ and a π^* both band providing the electron density of state around the Fermi level, giving the material its characteristic metallic behaviour, as it is displayed in Figure 4.4.1(b). Starting from the situation introduced for the metal band structure,



Figure 4.4.1: Band structure diagram of VO_2 in the insulating phase (a) and in the metallic one (b), according to the Goodenough model [7].

following Goodenough's idea, there are two features characterizing the band structure changes:

- 1. the raising of the π^* band above the Fermi level;
- 2. the splitting of the $d_{||}$ band into bonding and antibonding bands, so that no states remain around the Fermi level.

They both find good agreement with some structural changes which happen going from the rutile to the monoclinic lattice. The displacement of the vanadium atoms in the direction perpendicular to the rutile c-axis (so the zig-zag pattern) allows to explain the uplift of the π^* band to higher energies, since this distortion is responsible for important changes in the V-O bond distances. The second feature can be addressed to the dimerization process involving the vanadium atoms along the rutile c-axis, that occurs going from the high to the low-temperature phase of VO₂. The presence of bonds between vanadium atoms can explain the splitting of the $d_{||}$, previously not related to actual bonds between the metal atoms: this way the bonding band will decrease its energy, going below the Fermi level, while the antibonding one is moved at higher energies, above the bottom of the π^* band.

A simple way to see what happens across the transition is finally resumed: the zig-zag distortion brings the π^* band above the Fermi level, leaving the $d_{||}$ band half-occupied and, at the end, the V-V dimerization process splits this band in two parts, pushing below the Fermi level the full-occupied band, and raising the empty one above the Fermi level, opening a gap between the top of the $d_{||}$ band and the bottom of the π^* one.

4.5 Existing Results

Before proceeding with the next chapter about the experimental results, it can be useful to briefly introduce some existing experimental results concerning the lattice dynamics of vanadium dioxide. A deep inspection of the lattice dynamics of metallic VO_2 is needed in order to understand the role that a Peierls mechanism could actually have across the metal-insulator transition.

In 1970, Brewes introduced a free-energy expansion model, and together with relatively simple symmetry consideration connecting the two different structures involved in the transition, he did manage to find out that a lattice instability at the $\langle 101 \rangle$ zone-edge (that matches to the R point of the Brillouin zone) can be addressed as the responsible phenomenon leading the transition [35].

The first results about vanadium dioxide vibrational properties were obtained thanks to Raman scattering measurements. This technique is not perfectly suitable to produce a very detailed picture of the lattice dynamics, or better, it does not allow to get undeniable proofs supporting a Peierls mechanism based on the Brewes's model, but it permits to gather some precious hints about what happens inside vanadium dioxide. Srivastava and Chase inspected both the insulating and the metallic phases [36]. Their results reveal quite strong and sharp modes for the low-temperature phase, without any unusual temperature dependence of the positions, intensities and widths of the lines. On the other hand, the high-temperature phase mainly shows a strong and broad band, while the weaker lines expected for this phase are probably broadened. Thus, the principal conclusion of this work is the presence of heavily damped phonons in the metallic phase. Thanks to Schilbe [37], refinements of the



Figure 4.5.1: (a) Constant-**Q** IXS scans as a function of temperature for the R point. (b) Phonon dispersions from experimental results (points) and calculations (red and blue lines) [38].

Raman spectra were introduced, and he pointed out the similarities of the metallic phase spectra with TiO_2 results.

Until the end of 2014 there were not direct dispersion relation measurements; before the existence of the extreme powerful third generation synchrotron facilities, there was one insurmountable difficulty preventing the direct studies of phonon dispersions with neutrons, that is the large incoherent cross section of vanadium. Anyway, Budai et al. [38] provided the first direct results which are able to explain the role of lattice vibrations in VO₂. They did manage to supply a quite complete picture of the phonon landscape, together with valid ab initio calculations as displayed in Figure 4.5.1; here it is possible to see that softened phonons are found within the dispersion relations, and there is good agreement between the experimental data and the calculations results, even if the experiments reveal little lower energies with respect to the theoretical predictions. Then, Budai et al. pointed out the role of the soft mode at the R point of the Brillouin zone, underlining frequency dependence on temperature above the transition. Unusual large widths characterize the measured phonons, with very weak temperature dependence; according to Budai et al. this feature is to be addressed to the anharmonicity, that plays a very important role in VO_2 lattice dynamics [38]. Another interesting finding is about the role of the phonons within the entropy change across the transition: both experiments and calculations show that almost the 70% of this change is given by a phonon contribution, and most of the remaining 30% is due to the electrons, being any other contribution negligible (for example, from magnetism). To conclude, simulations have been carried out supporting the orbital polarization that takes place across the transition, an interesting feature that was previously discovered thanks to experimental results in 2005.

Chapter 5

Experimental Results

5.1 Sample Growth

The VO₂ single crystal was grown by P. Strobel and P. Rodierre at the Néel Institute (CNRS) of Grenoble, using the chemical vapour transport technique [39, 40]. The basic concept of this growth technique is the following: a condensed phase (usually solid in this case) does not have a sufficient pressure for its own volatilization, but it can be volatilized in the presence of a gaseous reactant, known as transport agent, which allows to deposit the starting material elsewhere in the form of crystals. In order to make this process feasible, it is necessary to have different external conditions for the chemical equilibrium at the two different positions of volatilization and crystallization: this is done by applying unequal temperatures for volatilization and crystallization. For a complete description of the vanadium dioxide growth, please refer to [41].

5.2 Some Details

Here both the IXS and the diffuse scattering results are reported and combined in order to give a full description of the lattice dynamics of vanadium dioxide.

Inelastic X-ray scattering measurements were performed at beam line ID28 at the ESRF. The Si (999) reflection order of the backscattering monochromator was used, which provides an incoming energy $E_i = 17.794 \, keV$ (corresponding to 0.6968 Åof incident wavelength) with an energy resolution $\Delta E_i \simeq 3.0 \, meV$. The multilayer setup has been exploited: in this configuration a multilayer system situated in the experimental hutch is used in conjunction with the cylindrical part of the toroidal mirror (placed in the optical hutch 3) in order to get a good focus in the horizontal and vertical direction, respectively, with a resulting beam size of approximately $50 \times 50 \,\mu m$. During the measurements analyzer number 2 was the one aligned with the 2θ angle, because it shows the best performances among the nine analyzers. It was aligned with the beam also during the second run of measurements, even if analyzer number 7 was out of business because of temperature control problems: the temperature was quite off of the elastic temperature, that means having the same temperature on both the analyzer and the main monochromator. Since we were only interested in acoustic phonons, the energy range of each scan was between $\pm 25.28 \,meV$, which corresponds to a temperature scan of the monochromator of $T_0 \pm 0.555 \,K$. The whole area of each scan was covered with 74 points and a variable counting time of 60, 75 and 90 s, where longer times were utilized for points out of high symmetry directions.

X-ray diffuse scattering data were taken on beam line ID23. Since other samples had to be measured, a common incident wavelength of 0.7 Å (very close to the value of ID28) was chosen, in order to be far enough to the fluorescence threshold. The beam dimensions at the sample position are $30 \,\mu m$ vertically and $40 \,\mu m$ horizontally. The sample is rotated over 360° with constant step of 0.1° , and for each step an image was acquired, with an exposure time of $0.1 \,s$ per image.

5.3 IXS Experiment

5.3.1 Preparation

Before starting with the real measurements, it was needed to prepare the experiment, which basically concerns the sample alignment. The vanadium dioxide single crystal, with needle shape, was mounted on a goniometer head, in order to be able to move it freely towards the desired geometrical configuration. After mounting the sample, the first step is to drive it in the center of rotation, so that rotating the sample along the z-axis (small theta angle, θ) it does not cause the sample to precess with respect to the incident X-ray beam. The next step consists in mounting the CCD camera and observe the diffraction signal from our VO₂ single crystal, in order to identify the two diffraction spots needed for the **UB** matrix construction: this matrix is able to reconstruct the reciprocal lattice, allowing to move across the reciprocal space and to take measurements in the desired regions [42].

After an initial inspection of the elastic diffraction from the room temperature



Figure 5.3.1: Photograph of the sample mounted on the goniometer head in its final geometry.

monoclinic phase, the temperature was increased to above the structural and MIT transitions by the use of a Oxford Cryostream 700 system [43], which uses a blow of nitrogen gas to increase the temperature of the sample: the nozzle of this apparatus was positioned at rust a few millimeters from the sample. Inspecting the diffraction pattern while changing the temperature allows for an approximation of the transition temperatures of our crystal, that in our case were about 339 K heating up, and 337 Kcooling down, showing just a couple of degrees of hysteresis. During the alignment of the tetragonal structure, the temperature was kept fixed at 350 K, and more than one manual adjustment action of the goniometer head was needed. The final geometry of the sample is displayed in Figure 5.3.1. In this configuration we were finally able to have the HHL plane accessible in the scattering plane, finding the $(1 \ 1 \ 1)$ and the (2 2 0) Bragg spots. At this point, everything is ready to start the measurements, and after deciding the zones of interest only one last thing has to be checked: in order to reach all the interesting points in the reciprocal space, different geometrical configurations of the entire experimental setup are obtained. Particular attention is needed not to cross the hard limits moving the instrumentation, where Figure 5.3.2 shows a schematic representation of the laboratory reference system [42].



Figure 5.3.2: Schematic representation of a 4-circle diffractometer [42].

5.3.2 First Run

During the first experiment, also taking advantage of a previous work done on TiO_2 [44], that shows an anomalous instability along the rutile A-M direction, we started taking data along the A-M direction, where the Brillouin zone is shown in Figure 5.3.3. The other direction initially inspected is the A-Z direction, being the most rel-



Figure 5.3.3: Brillouin zone of the rutile VO₂.

evant direction still unexplored. After the sample alignment, we started acquiring data at the temperature of 350 K, and a quite evident softening at the M point of the

Brillouin zone and in the middle of the A-Z direction have been found. This softening is displayed in Figure 5.3.4, where the first data already available during the experiment are presented. The main goal during this first experiment was to carry on a study as a function of temperature along these two directions: thus, we proceeded acquiring data at 400 K and very close to the transition temperature at 340 K, which means just one degree above the T_{MIT} of our sample. The data analysis mainly consists of two



Figure 5.3.4: Experimental points at 350 K along the A-M-A direction (a), and along the A-Z direction (b).

different step:

- 1. conversion of the temperature scale into an energy scale: indeed, the spectra resulting from the data acquisition, are given as a function of temperature at first. As already mentioned at the beginning of this chapter, the desired energy transfer range is achieved scanning the temperature of the backscattering monochromator. The high quality of the crystal allows to connect ΔT to ΔE with an excellent level of confidence, through the expansion coefficient $\alpha(T)$;
- 2. fit of the spectra: it allows to get the values of energy, width and intensity (with errors) for each spectrum, thus for each phonon.

At first sight, the results for the other two temperatures were in good agreement with the results presented in Figure 5.3.4, and after the data treatment it has been possible to plot the dispersion relations along the two directions studied, as we can see in Figure 5.3.5. In Figure 5.3.5(a) we can notice an energy lowering of about 8 meVat the M point, which corresponds to the scattering vector $Q = (2.5 \ 2.5 \ 1)$. Instead, in Figure 5.3.5(b) an energy softening is evident in the middle of the A-Z direction, at the point $Q = (2.25 \ 2.25 \ 1.5)$. In the latter dispersion relation, it does worth to underline that the points at H = 2.4 and H = 2.5 are not very trustful, since their behaviour does not fit perfectly with the general trend of the dispersion curve. This problem is due to the quality of the spectra at those Q-points, which were not of high quality, resulting in a difficult, but still exploitable, fit. From Figure 5.3.5, it is also possible to observe that a common tendency of energy decreasing is present, thus it can be useful to proceed with a direct inspect the spectra from which these data are extracted. A closer look of these results is displayed in Figure 5.3.6: here we show the temperature dependence of the measured high symmetry points of the Brillouin zone, and the spectra at the soft point between the A and Z points. It is clear that an energy softening occurs during the cooling down process for each Q-fixed scan, even if it can be pointed out that this energy lowering is quite modest. This is true, but we also need to take into account that the temperature range exploited in our study is not very wide, especially if we compare it with the temperature range considered by Budai et al. (more than 400 degrees!) [38]. Moreover, after a more accurate inspection, a very interesting feature can be highlighted: apart from the M point, both the A, Z and $Q = (2.25 \ 2.25 \ 1.5)$ points show a larger phonon energy softening going from 350 K to 340 K than between 400 K and 350 K (see Figure 5.3.6(e)).

Another particular issue can be revealed in all the spectra in Figure 5.3.6: energy scans at constant \mathbf{Q} show very broad phonon peaks (with an average value of the widths of about $5 \, meV$ over these twelve scans), and their shapes are well fitted by damped harmonic oscillator lines. These results are in quite good agreement with the model introduced by Budai *et al.*, where the lattice dynamics of vanadium dioxide is driven by an anharmonic mechanism, which leads to this stiffening with increasing temperature, and large phonon widths. Moreover, these broad peaks are almost temperature independent: this phenomena can be addressed to a competition between electron-phonon interactions (higher importance approaching the transition temperature) and increasing phonon-phonon coupling interactions on heating (anharmonicity).



Figure 5.3.5: Dispersion relations as a function of temperature with error bars, along the A-M-A direction (a) and the A-Z direction (b).


Figure 5.3.6: Constant-**Q** IXS scans as a function of temperature for the points Z (a), A (b), $Q = (2.25\ 2.25\ 1.5)$ (c) and Z (d). (e) Summary of the energies of these points as a function of temperature.

One last discussion about the intensities of spectra present in Figure 5.3.6 is needed; this is possible since there is just a constant shift between different spectra, leaving the height of the peak trustful for a comparison. Like for the energies, the M point shows an anomalous behaviour with respect the other points also for the intensities: approaching the transition temperature, the intensity characterizing this point decreases, leading us to think that it does not play a crucial role within the Peierls mechanism. On the other hand, the Z point does not reveal big changes with temperature, while both the A and the soft point situated in the middle way between A and Z, reveal an enhancement of intensity on decreasing the temperature. These last remarks match with the results reported about the R point of the Brillouin zone, meaning that the inspected points within this work, can also play an important role across the transition. It can be interesting to proceed showing directly the intensities along the A-Z direction, and their behaviour as a function of temperature: this is done in Figure 5.3.7. As previously noticed talking about the energies for the points with H values of 2.4 and 2.5, also the intensities are not completely trustful because of not perfect spectra (see also bigger error bars). Looking at the last mentioned plot, we can also notice that the intensity is quite higher in the middle of the A-Z direction $Q = (2.25 \ 2.25 \ 1.5)$, and this feature can be explained in two different ways:

- 1. there is a big softening driving the transition within the whole HK1.5 plane, which can be addressed to a soft line connecting the two R points of the Brillouin zone;
- 2. as suggested by DFT *ab initio* calculations, two degenerate phonons are present in that region [45].

It is important to underline that these values directly take into account the correction for the Bose. As explained in Chapter 2 the experimental intensity is roughly proportional to the term

$$n(E) + \frac{1}{2} \pm \frac{1}{2}$$

where n(E) represents the Bose occupation factor, the + sign stands for energy loss (phonon creation) and the - sign stands for energy gain (annihilation). Thus, considering the phonon creation process, the correction is obtained by dividing the experimental value of the intensity by the factor n(E) + 1. This way, it is possible remove the influence of the phonons population due to the temperature, getting a direct evaluation of the scattering function $S(\mathbf{Q}, \omega)$.



Figure 5.3.7: Intensity values with error bars obtained through the fitting process.

5.3.3 Second Run

During the second IXS experiment we mainly explored the line connecting the soft point in the middle of the A-Z direction and the M point and the line connecting always that soft point to the R point, together with a grid Q-points belonging to the HHL and the HK1.5 planes. The goal was to inspect these two different planes, searching for possible soft lines. Since there was not enough time to proceed with a complete study as a function of temperature, we decided to acquire these data at the temperature of 340 K, as it is the most interesting temperature, just one degree above the transition. Of course, the same procedure for data analysis has been followed after their acquisition. The first results are displayed in Figure 5.3.8, where the phonon energy variation across the HHL plane is presented. Unfortunately, some good points in the region delimited by H = 2.2 - 2.25 and L = 1.2 - 1.3 are missing, mainly because of bad quality spectra, which provide untrustworthy values. Apart from that zone, it is possible to observe the presence of a low energy line going from the M point, to the $Q = (2.25 \ 2.25 \ 1.5)$ point: it does not appear so clearly, but it is due to the intrinsic difference of in energy between the two soft points just cited. Indeed, it is possible to



Figure 5.3.8: Phonon energy landscape on HHL plane.

notice this feature within Figure 5.3.5(a) and (b), where we can identify an offset of almost 3 meV. Moreover, there exists one point along the soft line, which doesn't match perfectly with the others, even if it is obtained from a good quality spectrum; this is $Q = (2.3 \ 2.3 \ 1.4)$, with an energy of $13.008 \ meV$, slightly higher than the neighbors along the line. Anyway, apart from the soft point at $Q = (2.25 \ 2.25 \ 1.5)$, there are no evidences for these low energy phonons to play a significant role across the transition.

As previously introduced, the other studied plane is the HK1.5, and the output is revealed in Figure 5.3.9. Here the low energy phonons line is much more clear than what has been found for the HHL plane. This is not a really unexpected result, since this line lies in between of two R points (see Figure 5.3.3), where the main lattice instability that leads the transition is located. Thus, these results allow us to confirm that the high intensity revealed from the $Q = (2.25 \ 2.25 \ 1.5)$ point can be explained thanks to a soft line in the energy landscape of the HK1.5 plane. This feature can also bring to the following interpretation: the low energy phonons we are talking about, may be involved in the transition process, having energies comparable with the energy of the R point phonon and high intensities, which increase with deceasing



Figure 5.3.9: Phonon energy landscape on HK1.5 plane.

the temperature toward the T_{MIT} .

5.4 Thermal Diffuse Scattering

5.4.1 Preparation

In this case the preparation phase of the experiment is much faster with respect to the IXS experiment. Indeed, beam line ID23 is a highly automatized laboratory, where the only manual action is to place the sample on the appropriate sample-holder. The beam is centered thanks to a visual interface which exploits the fluorescence screen, and this is done using a standard sample, available inside the Experimental Hutch. The next step is to replace the standard sample with the sample we want to measure, and proceed with the automated procedure to find the center of rotation of the needle-like sample: this is simply done by clicking with the cursor on three different position of the screen (the process can be repeated a few times to be sure that the sample does not move off of the beam upon rotation). After selecting the parameters (such as exposure time, rotation velocity...) everything is ready to start the acquisition.

5.4.2 TDS Data

As above mentioned, the step width is 0.1° to get a full rotation of 360° for our vanadium dioxide needle; data are recorded for each step. As discussed in Chapter 2, with this technique it is possible to obtain classical information about the diffraction pattern together with diffuse scattering signal, which mainly contain information about the lattice vibrations of the system, in term of phonon intensities. After the experiment, data treatment consists in running reconstructions exploiting the data acquired, in order to get as final results pictures representing the intensity distribution across high symmetry planes in the reciprocal space. Figure 5.4.1(a) shows the



Figure 5.4.1: Thermal diffuse scattering across the HK0 plane at 340 K (a) and 295 K (b).

HK0 plane for the tetragonal structure just above the transition temperature, while in Figure 5.4.1 it is possible to visualize the plane corresponding to the rutile HK0 for the monoclinic phase. Here we use the HK0 label to name the monoclinic plane too (thus, the rutile reference system): this choice has been made mainly because our VO_2 sample was twinned in the M1 phase, making much more difficult to individuate the correct labels. Moreover, no direct interest is present to label each Bragg spot in the low temperature phase, since we do not have IXS results for a direct comparison. For what concern this plane, we did non measure directly this plane during the inelastic scattering experiment, but we can exploit the results presented by Budai *et al.* [38] for a brief discussion: even if they don't show a complete energy landscape (like in Figure 5.3.8 and 5.3.9) across the HK0 plane, the streaks prevailing in Figure 5.4.1 (for example between $(2 \ 0 \ 0)$ and $(0 \ 2 \ 0)$) can be addressed to strong TA mode along the $\Gamma - M$ direction. It is easy to see that this intense diffuse scattering signal becomes much weaker below the transition temperature, suggesting that the monoclinic structure is the stable one.

The second interesting plane is the HHL, which is displayed in Figure 5.4.2. As



Figure 5.4.2: Thermal diffuse scattering across the HHL plane at 340 K (a) and 295 K (b).

already explained, the rutile reference system is used to label the monoclinic structure too. The situation is very similar to the HK0 plane: here the TDS signal is a bit weaker even for the metallic phase, resulting in an almost complete disappearance of the diffuse scattering signal below the transition temperature, in perfect agreement with the results revealed by Figure 5.4.1. This time it is possible to do a direct comparison between the diffuse and inelastic scattering experimental data. The highlighted zone in Figure 5.4.2(a) represents the region displayed in Figure 5.3.8: the intensity distribution is in very good agreement with the phonons energy landscape, proving that the low energy phonons that possess these high intensities are responsible for the diffuse scattering pattern revealed in Figure 5.4.2(a). Thus, even if these specific phonons are not directly involved within the transition process, it is possible to notice the presence of strong vibrations across the whole intensity pattern of the metallic phase. Proceeding with the analysis of the results, it is interesting to show



Figure 5.4.3: TDS data across the HK1.5 plane at 340K.

the thermal diffuse scattering pattern across the HK1.5 plane (see Figure 5.4.3). The white circle surrounds the area studied also with the IXS technique, and the high intensities line perfectly matches with the soft line present in the energy landscape of Figure 5.3.9. Moreover, as previously mentioned, the phonons populating this region can play an important role for the transition, having a similar behaviour as the R point (darkest zone inside the white circle) of the Brillouin zone.

Chapter 6

Conclusions

As a starting point it is useful to resume the main points of the experimental results:

- the thermal diffuse scattering above and below the T_{MIT} shows instability in the tetragonal structure with intense signal across all the high symmetry (and not) planes. This general instability of the structure disappears in the insulating phase, revealing just weak TDS signal below 337 K;
- anomalous energy softening in the lattice dynamics of the metallic phase, exhibiting soft lines in the energy landscape of the HHL and HK1.5 planes, that suggest strong lattice instability. These measurements are in very good agreement with the TDS results, proving that the low energy phonons are responsible for the diffuse scattering too;
- hardening of the phonon energy with increasing temperature (stronger for the 340 350 K step) testify that anharmonicity plays an important role within the lattice dynamics processes in the metallic phase;
- an accurate analysis of the intensities reveals that for the points A, Z and $Q = (2.25\ 2.25\ 1.5)$, the signal gets stronger approaching the transition temperature $(340 350\ K$ with respect $400\ K$). It suggests that these vibrations, together with the whole soft line lying on the HK1.5 plane, can play a role across the transition. Nevertheless, the most interesting point remains the soft point in the middle of the A-Z direction, since its intensity is much stronger than the neighbors intensities.

Of course, the last point represents the most interesting result among the others. Unfortunately, we did not manage to get good quality *ab initio* calculations: the simulations produced a lot of negative energy phonon modes, and it can probably be addressed to the anharmonicity characterizing VO₂ lattice dynamics. Thus, to perform a direct comparison with the experimental data and to represent the normal modes, it is mandatory to exploit existing results. A very interesting feature is the lack of agreement between the experimental data and the calculations along the A-Z direction [45] (not displayed by Budai *et al.* [38]). Indeed, if we look at the dispersion relations obtained by the DFT method, just a weak energy softening of about 1 - 1.5 meV is revealed in the middle of the A-Z direction, while the experimental results show a decrease of 3-4 meV. Instead, looking at the DFT+U calculations, which better describe the lattice dynamics of the rutile VO₂, the softening is completely absent. In contrast, the results presented by Budai *et al.*, show that experimental points and *ab initio* phonon dispersions are in good agreement, apart from a constant energy shift: this means that existing calculations are not able to predict properly the energy softening at Q = (2.25 2.25 1.5).

At this point it can be useful to introduce a few information about the phonon eigenvectors, through their graphical representation within the rutile unit cell. This is done in Figure 6.0.1, where the normal modes at $\mathbf{q} = \mathbf{A}$ and Z are displayed. Figure 6.0.1(e) shows the linear combination of the two degenerate modes at the R point of the Brillouin zone, where two softened phonons are enough to explain both the vanadium atoms dimerization and the zig-zag pattern happening in the monoclinic structure. It is true that they are enough to explain these features, but the lattice instability at this point has been labelled as the only responsible for the transition so far. Nevertheless, from Figure 6.0.1(a), (b), (c) and (d) it is possible to see that the two degenerate acoustic modes at both A and Z points may represent a contribution to the dimerization process across the transition, supported by the results previously discussed. Unfortunately, no information about the soft point in the middle of the A-Z direction are available, thus remaining unrevealed the actual role across the transition for these phonon modes.

The most important features of our study are the following:

- anomalous softened phonons;
- higher phonon intensities decreasing the temperature;
- intense thermal diffuse scattering in the metallic phase, disappearing below the transition.



Figure 6.0.1: Normal phonon modes at $\mathbf{q} = \mathbf{A}$ and Z. (a), (b) Two degenerate modes at $\mathbf{q} = \mathbf{A}$. (c), (d) Two degenerate modes at $\mathbf{q} = \mathbf{Z}$. (e) Linear combination of the two degenerate modes at $\mathbf{q} = \mathbf{R}$. The blue and red balls represent vanadium and oxygen atoms, respectively [45].

All these results describing the vanadium dioxide metallic phase, reveal that structural instabilities play an important role across the metal-insulator transition. Thus, our study together with the results by Budai et al. give unambiguous proves that a Peierls mechanism is in part responsible for the gap opening going from the high temperature tetragonal structure, to the low temperature monoclinic structure. Even if the conclusions provided by the lattice dynamics studies are quite exhaustive, it is not possible to assert that a lattice instability is the only responsible for the transition; as previously discussed a Mott mechanism can be considered. The work done by Haverkort *et al.* is very clear in explaining the role that an electronic correlation can play in the process we are talking about [46]. It is helpful to briefly resume their work, in order to introduce one final idea about the metal-insulator triggering mechanism. The VO₂sample has been studied using the X-ray absorption spectroscopy (XAS) technique, in order to study the vanadium $L_{2,3}$ edges with different light polarization, in both the metallic and insulating phases. Inspecting the spectra it is possible to notice that the polarization affects the spectra in the monoclinic structure, while the rutile structure is almost independent on the polarization of the incident light. Thus these features reveal that the vanadium 3d orbitals are almost isotropically occupied in the metallic phase, while they are not below the transition temperature. Completing these studies with simulations and following the formalism of decomposing the orbitals into three different parts (σ , π , δ), it is possible to obtain the following results:

- in the monoclinic structure, the orbitals have a strong σ character, while the π and δ parts are almost unoccupied;
- in the rutile structure the orbitals are indeed almost isotropically occupied.

This orbital polarization change across the transition can take place only considering the role of the strong electron correlation within the system under study, thus a Mott mechanism has to be taken into account.

This, of course, doesn't mean that the Peierls process plays a weaker role than the Mott one, but it probably means that the two different mechanisms cooperate to lead the metal-insulator transition. One possible idea, that is becoming more likely with the recent results about lattice dynamics, is that the electron correlation starting the orbital polarization triggers the Peierls mechanism. This model exploits the electron-electron interaction to bring the starting three-dimensional system to an almost one-dimensional system, being in quite good agreement with the discussion at the end of Chapter 4. A better model of the system, in order to perform trustful ab *initio* calculations, should be developed, since it will provide an enormous help to understand the importance of the mode at $Q = (2.25 \ 2.25 \ 1.5)$ and the role of the whole soft line on the HK1.5 across the metal-insulator transition.

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