Studies of the Quantum Phase Transition in Chromium Using Inelastic X-Ray Scattering and Ab Initio Methods

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STUDIES OF THE QUANTUM PHASE TRANSITION IN CHROMIUM USING INELASTIC X-RAY SCATTERING AND AB INITIO METHODS

by

Chengyang Li

A dissertation submitted to the Graduate College
in partial fulfillment of the requirement
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In this project, inelastic x-ray scattering (IXS) was used to measure the phonon dispersion in chromium at high pressure and low temperature, and an ab initio method was used to simulate the phonon dispersion with different lattice constants and magnetic orders. The IXS measurements were carried out in Sector 30 at the Advanced Photon Source at Argonne National Laboratory. Data were taken at room temperature with pressures of 1.29 GPa, 8.15 GPa, 10.6 GPa, and at 5 K with a pressure of 18.36 GPa. The data shows similar phonon behavior in the antiferromagnetism (AFM) and the spin density wave (SDW) states at room temperature, but different phonon behavior at 5 K and 18.6 GPa. The ab initio simulation was used to calculate the phonon dispersion with AFM plus SDW at the lattice constant corresponding to the measured pressure in the experiment. By comparing the experimental data and the simulation result, it seems likely that a new state exists after the quantum phase transition.
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CHAPTER I

INTRODUCTION

In this thesis, Inelastic X-ray Scattering (IXS) and ab-initio calculations with Density Functional Theory (DFT) are used to probe the Quantum Phase Transition (QPT). Single crystal chromium is used as the sample because it is the simplest system to show this transition under high pressure and low temperature. Quantum Espresso simulation software [1] was used to calculate the phonon dispersion in chromium with different magnetic structures. Comparing the experimental data and simulation result are carried out to understand the QPT.

A quantum critical point (QCP) is a special type of phase transition due to quantum fluctuation, which occurs at zero temperature. However, a QCP can affect the behavior of a material over a wide range of temperature. The QCP can be driven by changing parameters such as pressure or magnetic field. Many of the most interesting systems being studied for fundamental science and for technological applications (e.g., high temperature superconductors, transition metal oxides, colossal magnetoresistance manganites) appear to be close to a QCP. However, the complexity of many of these systems makes data interpretation difficult.
Chromium is a transition metal with many fascinating properties. It exhibits antiferromagnetic (AFM) ordering with a Spin Density Wave (SDW) state at room temperature. Above its Néel temperature of 311K, Cr transforms to paramagnetic state. In recent years, Cr has attracted the attention of many experimentalists and theorists. Studies of magnetic ordering \[2\] showed that Cr is close to a QCP at zero temperature, making it one of the simplest known systems to show this behavior.

High-energy-resolution inelastic x-ray scattering is used to study the QCP by measuring changes in the phonon energies above and below the critical pressure. It is necessary to use high-pressure techniques to reach the QCP. The narrow energy range of the changes in the transition requires a high-energy-resolution spectrometer to study the phenomena.

The phonon dispersion below and above the critical point has been measured for Cr in a diamond anvil cell (DAC) and the phonon dispersion across the pressure-altered Néel temperature at low temperature has been studied. When the temperature changes over a wide range, the anomaly in the phonon dispersion along (100) direction shows different softening in the antiferromagnetic state and paramagnetic state \[3\]. The comparison between the experimental and computational phonon dispersion with non-spin and AFM plus SDW structure will help us understand the real influence of the quantum phase transition in chromium at high pressure and low temperature.
Phonon dispersion calculations have been carried out by using Density Functional Theory (DFT) as implemented in the Quantum Espresso codes to look for phonon anomalies close to the critical pressure and Néel temperature. The comparison between the simulation of the paramagnetic and antiferromagnetic structure points out different behavior in the phonon dispersion. A simplified SDW model has also been simulated and reveals the stability of this structure in the classical regime. However, the experimental data across the QCP shows a surprising result. The phonon dispersion does not agree with any model when it approaches to the boundary of the first Brillouin zone. It may indicate there is a new state after QPT, which may be a quantum paramagnetic state.
CHAPTER II

QUANTUM PHASE TRANSITION

2.1 Introduction to Quantum Phase Transitions (QPT)

In recent years, Quantum Phase Transition (QPT) has become an important research branch. This kind of phase transition has brought a brand-new mechanism and insight to investigate physical phenomena, which is hard to understand and study with traditional methods. The specific conditions needed to access the quantum phase transition necessitate the use of the techniques to achieve extreme environments.

A QPT is a phase transition that occurs at zero temperature between quantum states. This transition is different from a classical phase transition because it is not driven by thermal fluctuations. This independence from the thermal force requires us to inspect the variation of the ground state in the system.

Define a Hamiltonian $H(g)$ in a lattice involving all the degrees of freedom and a function $g$ by varying with a parameter such as pressure, chemical doping and magnetic field. The solution of the ground state energy $H(g)$ is analytic when it depends on the function $g$. However, this dependence is not fixed all the time. Nonalalytic solutions may exist in both the finite and infinite lattice [4] and these
solutions will not follow the classical theory. The reason is if the energy is a conserved quantity, the incomplete dependence on the function \( g \) in the Hamiltonian will have a separate term from the function \( H_0 \) and must commute with the dependant term \( H_1(g) \).

\[
H(g) = H_0 + H_1(g) \tag{1.1}
\]

The commuted terms result in the level crossing and avoided crossing in the ground state, and at last produce the nonalalyticity in the ground state of the Hamiltonian, which brings a quantum phase transition.

A classical phase transition is driven by thermal fluctuation, and the variation of the temperature drives the alternation of the states. Therefore, the classical theory can not be utilized in the quantum theory because the thermal energy is zero at absolute zero temperature. The concept of quantum energy solves the problem. The momentary change of the quantum energy in the lattices is driven by quantum fluctuations, which are determined by the Heisenberg uncertainty principle. Although thermal fluctuation is not the driving force of the QPT, there are some other elements which can affect the quantum fluctuation at zero temperature, such as pressure, external magnetic field or chemical composition (doping). Instead of varying the temperature, studying the continuous variation of these elements provides a method to observe the phase transition in the classical and quantum regime.
In a QPT, a quantum critical point (QCP) is defined as a special point at zero temperature, which is invariant even when the other elements are changed. It means there is a critical point $g_c$ in the function $g$. In this point, the ground state energy of the Hamiltonian $H(g)$ is conserved.

$$g = g_c$$

Figure 1

A QCP exists at zero temperature, $g$ is the function that can access the quantum phase transition such as pressure, inverse pressure or magnetic field. Quantum criticality can extend far from the QCP. In contrast, above or below the temperature in which a classical phase transition occurs, the effect of classical criticality still exists, but it is limited to a very small temperature range and disappears soon with the
shift of the temperature. The QCP occurs at the point $g=g_c$, is the critical value of the function $g$.

When the function $g$ approaches the critical point $g_c$, the competition of quantum and thermal fluctuation determines the classical and quantum regime. There are two kinds of transitions in a classical phase transition; a first order transition has a discontinuity at some temperature, while a second-order phase transition will have a continuously varying first derivative of the energy but be discontinuous in the second derivative. A second order phase transition exhibits critical phenomena (also called classical criticality) in a confined range of parameters around the phase transition. However, the effect of a quantum critical point can be different from the effect of a classical critical point, which occur over a wide region in the function $g$ from the QCP even if the temperature is not zero. This phenomenon called quantum criticality, and the quantum critical regime $|g - g_c| > 0$ spreads above the QCP.

$$|g - g_c| > 0 \quad (1.3)$$

A quantum-fluctuation-driven transition occurs in this regime, when the quantum energy is larger than the thermal energy. The behavior of the quantum criticality is determined by variation of the quantum energy. When the temperature reaches the threshold and the thermal fluctuations drive the transition, the transition becomes a classical phase transition.
The concept of quantum criticality helps us to understand many experiments. The Ising chain near a QCP has shown that magnetic orders changed from ferromagnet to quantum paramagnet by applying magnetic field in the transition [5]. Thallium copper chloride TlCuCl$_3$ exhibits a QCP when it transforms from a Néel antiferromagnet to a quantum paramagnet by increasing pressure [6]. The high-pressure resistivity experiment on pure chromium shows that the spin-density-wave magnetism is suppressed when the pressure reaches the critical point [7]. BaFe$_2$ (As$_{1-x}$P$_x$)$_2$ has a sharp peak in the zero-temperature penetration depth arising from the quantum criticality [8]. The quasi-one-dimensional organic Bechgaard salt (TMTSF)$_2$ PF$_6$ has a similar resistivity, where the electrical resistivity is proportional to the temperature at a very low temperature at the critical point pressure [9-10]. The high-temperature superconductor La$_{2-x}$ Sr$_x$ CuO$_4$ shows evidence of quantum criticality when measuring the low-temperature in-plane resistivity of the doped single crystal with high magnetic fields [11].

Most of these materials have complex compositions and crystal structures, which complicate the understanding of the basic phenomenon. Therefore when we want to study some fundamental properties of a quantum phase transition, a simple system, is required for a convenient and accurate investigation. The spin and charge ordering in the pure chromium has been studied and the QPT occurs with a reorganization of the density-wave order [12].
Pedrazzini and Jaccarda reported that the spin-density-wave magnetism in chromium is suppressed at a critical pressure close to 10GPa at room temperature [7]. Spin and charge ordering is suppressed in the itinerant antiferromagnet with pressure according to recent work [5]. A weak coupling ground state and magnetic excitations coexisting above the Néel temperature leads to a collective slow mode around certain Q-points [6] and these modes will drive a quantum phase transition at sufficiently high pressures. An x-ray diffraction experiment shows the lattice constant of chromium is proportional to the inverse pressure; the increasing pressure will suppress the constant linearly, and results in a suppression of the Néel temperature [13]. Another x-ray diffraction experiment studied the evolution of the incommensurate ordering vector by measuring the spin and charge diffraction intensities. Although both the pressure and doping can drive quantum the QCP, the equally rapid variation of an ordering vector from doping are clearly different from the slow variation from pressure, which the vector changed very slowly above 4GPa. The experimental result demonstrates a clear weakly coupled BCS-type ground state, which coexists with the high-energy excitations above the ordering temperature in chromium [14]. Although these experiments do not reach the QCP, they reveal that a transition state may exist between the normal AFM state and quantum state, where the ordering and structure in chromium would be different. Further study of the chromium at QCP shows a threshold at 7 GPa where the mean-field BCS-like
exponential ground state breaks down which can describe well the spin density wave at low temperature. The mean-field ground state is continuously suppressed by quantum critical fluctuations for pressure above 10GPa, and a quantum critical behavior is considered around the critical point [15]. The whole process gives us an interesting result which delineates the quantum transition and we can choose the appropriate pressure point to detect the transformation of these states.

In these experiments, the magnetic structure in chromium is an important issue to understand the QPT in chromium, and the spin density wave is the sign of this structure. By studying the evolution of the magnetic order during the QPT, we can find a path to explain the behavior in chromium.

2.2 Spin density wave (SDW)

Spin density wave (SDW) is a low energy state of the solid with special ordering which is characterized by a periodic modulation of the spin density [16]. In 1960, Overhauser conjectured that the SDW would affect the directions of the local spins [17], and soon he suggested that the SDW in chromium combines with the antiferromagnetism [18-19]. The effect of SDW is usually revealed in a long length-scale in the super-structure, such as the SDW in chromium which is 28 times the length of the lattice constant at 311K [20-21]. Intuitively speaking it is suspicious that the effect in a long length-scale can influence a small cell in the short length-scale
too much, but the Fermi surface of the material has a relation with the spin density and then the periodicity of density wave of is connected to the Fermi surface vector. Some material with high spin density may have a nesting vector of the Fermi surface which is a vector in the reciprocal space between the electron pocket and hole pocket [22] in the first Brillouin zone.
(a) The projection on the z-axis of a spin density wave in a half period.
(b) The different directions of the spins in a spin density wave in the real space. (c) Bottom view of a spin density wave, perpendicular to the x-y plane.

When we observe the spins in a SDW only in the z-x or z-y plane, the wave shows the periodic modulation by the length and directions of the spins. In real space, it is easy to understand that the magnitude of the spins in a plane is only the projection of the spins on the z-axis, the view in the x-y plane of the real wave looks like a clock and the direction of the spins are the hands in a circle.

The SDW in chromium with antiferromagnetism is more complicated. The corner atom and the center atoms have opposite spins and the magnitude of the spins in the z-axis is changing gradually. There is another domain for this structure, which separates two areas with vertical propagation direction in the real space and has a transfer of the intensity between the satellites and another transfer in reciprocal space [23].

In chromium, there is a spin-flip transition at 123 K [24]. Above this temperature, the structure is a transverse SDW, where the directions of the spins are perpendicular to the wave propagation direction. Below this temperature, the structure becomes a longitudinal SDW, and the spin directions are parallel to the wave propagation direction. The spin-flip transition is a first order transition. It can be
described with the Landau theory in terms of coupling to the spontaneous strain [25].

The SDW drives a magnetostrictive coupling and a spin-independent electron-strain coupling.

![Figure 3](image)

Two kinds of SDW in antiferromagnetic chromium (a) Transverse spin density wave (b) Longitudinal spin density wave.

2.3 The SDW and QPT in chromium

As a transition metal, chromium has a simple bcc structure, which contains incommensurate antiferromagnetism with a SDW when the temperature is lower than
Néel temperature 311K. The spin-flip transition occurs at 123K, and the antiferromagnetic state during this transition is not changed. The amplitude of the density-wave order parameter is reduced when the temperature approaches the Néel temperature at low pressure, and it is further reduced when it approaches the QCP [26]. These interesting behaviors attracted many experimentalists and theorists to study the evolution of the states and the density-wave orders around the QCP.

The phase transition in chromium, TSDW = Transverse spin density wave, LSDW = Longitudinal spin density wave.
A study of magnetic ordering in the zero-temperature limit showed chromium exhibits quantum critical behavior, whose effect is not limited to very small range close to zero but also extends to higher temperature [2]. This phenomenon reminds us chromium is a good system to understand the QPT because the quantum critical regime in chromium can be accessible by pressure or doping. The simple metallic structure is convenient for analyzing the QPT mechanism.

The study of the ordering parameter near the QCP in chromium is implemented by measuring the intensity and wave vector of the SDW at high pressure [12]. Because of the limit of instrumental resolution, the state after the quantum phase transition is not probed. In order to explore the unknown area, measuring the phonon dispersion in chromium after the QCP is implemented because the change of the magnetic order can influence the phonon. As a comparison, the phonon dispersion in the different structures is simulated. The comparison between the simulation and the experimental data can help us to distinguish the evolution of the magnetic ordering from the other effects.
CHAPTER III

DENSITY FUNCTION THEORY

3.1 Introduction to Density Functional Theory (DFT)

Density Functional Theory is a quantum mechanical model to deal with the many-body system problem, and it mainly works on the ground state of the electronic structure. Instead of solving every electron’s function in a system with many electrons, this theory uses the concept of electron density to describe the properties of the whole system. This makes it very simple and easy to study the states by mathematical methods in condensed matter physics, quantum physics and computational chemistry.

In 1960, Hohenberg, Kohn and Sham established the foundation of the theory [27-28]. Firstly, the external potential $V_{\text{ext}}(r)$ of an electron system is determined exclusively, and it is a constant in the ground state. Secondly, the function of the whole system energy $E(n)$ is defined in terms of the electron density $n(r)$. The ground state energy is the same as the minimum of the function, so we can solve the ground state problem by calculating the minimum value. Thirdly, the ground state in an interacting system can equal the ground state in a supposed non-interacting system with a local effective potential. After these three steps, we can change the electronic
structure problem from solving a many-body problem to solving a non-interacting-system-density problem, which is much easier for numerical algorithms.

In a many-body system with electrons \( \{r_i\} \) and nuclei \( \{R_j\} \), the Hamiltonian is expressed as

\[
\hat{H} = \frac{\hbar^2}{2m} \sum_i \nabla^2 i + \sum_{i,j} \frac{Z_i e^2}{|r_i - R_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} - \sum_j \frac{\hbar^2}{2M_j} \nabla^2 j + \sum_{j,j} \frac{e^2}{|R_j - R_j|} \tag{3.1}
\]

The first three terms are the electronic terms and the other two terms are nuclei terms. It is easy to understand that since the mass of electron and nuclei have a large difference, separating the two terms could be a reasonable approximation. Meanwhile, the point charge in the system can be considered as a fixed potential. Then the whole problem becomes two problems: the electronic problem and the nuclei problem, which is the famous Born-Oppenheimer approximation [29]. The simplified Hamiltonian is

\[
\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{\text{nc}} \tag{3.2}
\]

where \( \hat{T} \) is the kinetic energy, \( \hat{V}_{\text{ext}} \) is the external potential acting on the electrons from the nuclei, \( \hat{V}_{\text{int}} \) is the interaction among the electrons, \( E_{\text{nc}} \) is the
energy of the nuclei. Now we need to solve the Schrödinger equation of the many-body system

\[ \hat{H}\Psi = E\Psi \]  \hspace{1cm} (3.3)

where \( E \) is the ground energy of the system in the external potential. When we deal with the electron wavefunction of the system, the concept of electron density is used in the problem [30]

\[ n(r) = N \sum_{x_1} \cdots \sum_{x_N} \int dr_1 \int dr_2 \cdots \int dr_N |\Psi(r, \cdots, r_N, s, \cdots, s_N)|^2 \]  \hspace{1cm} (3.4)

\[ n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle \]  \hspace{1cm} (3.5)

\[ \hat{n}(r) = \sum_i \delta(r - r_i) \]  \hspace{1cm} (3.6)

The expectation value of the electron density is \( \hat{n}(r) \), \( s \) is the spin variable.

Then the total number of the electrons is

\[ N = \int n(r) d^3r \]  \hspace{1cm} (3.7)

From the Schrödinger equation we can get the ground state energy \( E \) of this system by calculating the expectation value of the Hamiltonian, and the ground state wavefunction \( \Psi_0 \) determines the minimum of the ground state energy.

\[ E = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3r V_{\text{ext}}(r)n(r) \]  \hspace{1cm} (3.8)
A dramatic paper of Hoenberg-Kohn theorem was released in 1964 [27]. The two main points promote DFT as an exact theory for the many-body problem, the uniqueness of the external potential $V_{\text{ext}}(r)$ and the determination of the electron density in the universal function $E(n)$. The Hamiltonian can be written as

$$
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} 
$$

(3.10)

Then the energy function can be expressed with the density as

$$
E_{\text{KS}}[n(r)] = T[n(r)] + E_{\text{int}}[n(r)] + \int d^3r V_{\text{ext}}(r)n(r) + E_{\text{nc}}
$$

(3.11)

The kinetic energy and the electron-electron interaction are a general function of the density. A further hypothesis from Kohn and Sham [28] proposed the equivalence of the ground state density between an interacting system and a non-interacting system. The Hamiltonian of a non-interacting system has the kinetic energy and a local effective potential,

$$
H_{ks}(r) = -\frac{1}{2} \nabla^2 + V_{ks}(r)
$$

(3.12)

The density of this non-interacting system can be written as

$$
n(r) = \sum_s \sum_{i=1,N} |\psi_i^s(r)|^2
$$

(3.13)

The kinetic energy and electronic Coulomb energy (Hartree energy) can be expressed as
Then the Kohn and Sham equation is changed from H-K equation to

\[ E_{KS}[n] = T_s + E_{Hartree}[n] + \int d^3n(r)V_{xc}(r) + E_{xc}[n] + E_{xc} \]  

(3.16)

and the potential of the Kohn and Sham equation is

\[ V_{KS}(r) = V_{xc}(r) + V_{Hartree}(r) + V_{xc}(r) \]  

(3.17)

where the electron-electron interaction term is divided into two terms, Coulomb energy and the exchange and correlation energy \( E_{xc} \), the latter one has a different approximation. It equals the sum of the contribution from every independent single electron, which act separately on the density except they do not act on themselves. This is also called the Local Density Approximation (LDA).

\[ E_{xc}^{LD} = \int d^3r n(r) e_{xc}[n] \]  

(3.18)

where \( e_{xc}[n] \) is the exchange and correlation energy per electron.

There are some other approximations to solve the exchange and correlation energy. For the spin-polarized system, the local spin density is composed of two different densities and the sum is the total density. The new exchange and correlation energy includes the separate extension and the correlation of LDA from these two
densities, which is called the Local Spin-Density Approximation (LSDA) [31-32]. Instead of approximating the local density as the real density, another method can improve the result of LDA, which is called Generalized Gradient Approximation (GGA). It considers the gradient of the electron density to solve the problem where there is rapid change of the density [33].

With these approximations, and the separations of the kinetic energy and the Coulomb energy, the calculation of the electronic wavefunction and electronic eigenenergy can be carried out with an efficient numerical algorithm, which provides us a remarkable theory to study the ground state properties of the electronic structure. Although in the excited states, DFT does not perform as well as in the ground state, partial perturbation problems close to the ground state are still solvable. Accompanied by fast development of computer software and hardware, the simulation of the materials based on the software with DFT is becoming popular.

3.2 Quantum Espresso

Quantum Espresso (QE) is an integrated suite of computer code for simulating a material’s structures and solving the electronic-structure problems [1]. This software is composed of DFT, plane wave and pseudopotential parts. Espresso is the acronym of opEn Source Package for Research in Electronic Structure, Simulation, and Optimization. This is free software for all-level users under the GNU General
Public License and developed by the scientists in this project. QE can calculate ab-initio molecular dynamics, spectroscopic properties, response properties, structural optimization, and ground-state properties. The serial version of QE in Linux can solve most simple problems. The parallel version of QE can work on many different platforms. This version is very useful for high load calculation when the problem is complicated and needs many nodes or cores to run together.

In the last section, the general theory of DFT was presented. When we try to solve a real problem with DFT, such as describing the electronic structure of a metal, we need to choose a kind of basis set to characterize the space. Meanwhile, an efficient method is required for the convergence because the all-electron calculation is expensive. In QE, the plane-wave basis sets and pseudopotential are utilized to achieve this objective.

A plane wave has a constant frequency, whose wave fronts are parallel to each other and the propagation direction is perpendicular to these planes. In a periodic system, we can get the plane wave by Bloch’s Theorem.

\[ \psi_k(r) = e^{ik \cdot r} u_k(r) \]  \hspace{1cm} (3.19)

where \( k \) is a reciprocal lattice vector, \( u_k \) is a periodic function of the system such that

\[ u_k(r) = u_k(r+R) \]  \hspace{1cm} (3.20)
From the function, we use Fourier analysis and extend it to the three dimensions. We assume there is a set of plane waves

\[ u_k(r) = \frac{1}{N} \sum_G c_k e^{iG \cdot r} \]  

(3.21)

where \( G \) is a set of reciprocal lattice vectors, and \( c_k \) is the coefficient, then the wave function of the plane wave changes to

\[ \psi_k(r) = \frac{1}{N} \sum_G c_k e^{(G+iG) \cdot r} \]  

(3.22)

In a periodic system, the set of the plane waves in the reciprocal space is discrete and there are infinite points. However, in a practical problem we only need to get good accuracy, it means a reasonable range of values in three dimensions will be needed to solve the wave functions. The cut-off energy sets the limit, and this threshold will reduce all the unnecessary components.

\[ \frac{\hbar^2 (k+G)^2}{2m} \leq E \]  

(3.23)

As the name implies, the pseudopotential is not a real potential, but an auxiliary potential to reduce the computation cost. When we try to run the self-consistent calculation, although we have used the cut-off energy, the atoms with d and f orbit or higher orbits still have too many electrons so they will have a very large cost. It is natural to use the idea that the core electrons can be treated as the same as
the nuclei, which is regarded as a ‘larger’ core. The valence electrons are what we really need to calculate precisely.

There are two widely used methods to construct the pseudopotential in the first principle study. Norm-Conservation pseudopotential (NCPP) was proposed by Hamann, Schluter, and Chiang in 1979 [34-35]. They assumed the exact eigenvalue and nodeless eigenfunction are the same as the atomic wave functions beyond a cut-off radius $r_c$, and the norm of the pseudo-wavefunctions is the same as the all-electron wavefunction inside this atomic sphere. Meanwhile, to satisfy the transferability of the pseudopotential, the logarithmic derivatives of the exact and auxiliary potential should agree outside the core range. The transferability reduces with an increasing radius, but a larger radius can soften the pseudo-wavefunctions and accelerate the convergence. However, NCPP is still too ‘hard’. It needs large plane-wave basis sets for the first row transition metals, which mean a high-energy cutoff is required. David Vanderbilt developed the Ultrasoft pseudopotential (USPP) in 1990 [36]. USPP is charge-state dependant and abandons the norm conservation. This method produces much smooth and highly transferable pseudo-wavefunctions, thereby reducing further the requirement of the plane-wave basis sets.
3.3 Simulating a structure

The construction of a structure in QE has several basic components, and an accurate simulation requires more constraints to perform the details. The rationality of a structural model should be validated under different conditions including the energy threshold and k-points. All the properties are based on the calculation of wavefunctions, which comes from a self-consistent calculation after constructing the structure.

The fundamental frame of a structure is the atoms’ properties and the type of Bravais lattice. The structure is introduced by describing a unit cell, but a supercell can be used if it is needed. It is easy to give the total number of the atoms, but the same element may have a different structure if they have a different spin direction or chemical bond. There are fourteen kinds of Bravais lattices in three dimensions and setting up the lattice constants in every dimension and the angles between every dimension, we can get a general imagine of the cell. The spin information is required if a magnetic material is simulated. For metal, it is essential to smear occupations by some different functions, which can speed up the convergence and reduce the cost. The atomic species indicate the pseudopotential. The atomic positions are the most significant in the self-consistent calculation that determine the microscopic properties, and a small displacement of the atoms often brings some unusual phenomenon and properties.
How to get a rapid and excellent convergence is a challenge after we have constructed a unit cell. The cut-off energy is easy to start with a low value but it is important to execute more tests for a good convergence. The calculated total force and stress is a comparatively precise standard in that a balanced and reasonable structure always has a very small force and stress. The relaxation of the structure should be carried out if the output does not show all the atoms’ positions are stable and it is essential for an intricate structure k-points are an important component, which determine the exact numbers of wavefunctions to be calculated. The practical cost can be estimated by comparing results with different number of k-points. These are either produced automatically or pre-produced from QE’s special code and a large grid of k-points means much larger time consumption.

After acquiring the set of the wave functions, there are many properties that can be calculated subsequently such as the density of states, Raman cross-sections, X-ray absorption spectrum and the full phonon dispersion. The phonon frequency requires the inter-atomic constants, and the constants come from the dynamical matrix, which costs the most of all the steps. The full phonon dispersion of a structure with more than 10 atoms may need several weeks or even months in a middling cluster and a powerful PC cannot handle this scale but a simpler simulation is feasible.
CHAPTER IV

INELASTIC X-RAY SCATTERING

4.1 X-ray scattering

X-ray scattering is a widely used technique which includes many branches such as small-angle x-ray scattering, resonant or nonresonant inelastic x-ray scattering, x-ray Raman scattering and the most widely used technique, x-ray diffraction. This nondestructive method can determine the crystal structure, physical properties of the materials and the chemical compositions of some complex compounds. Usually when we choose a designed incident x-ray beam to hit a sample, the measurement of the scattered beam intensity will contain the information we hope to know.

There is a simple diagram, which shows a universal scattering process in Figure 5. The incident and scattering beam energy are defined as $E_i$ and $E_f$, the momenta of the beams are defined as $k_i$ and $k_f$, and the polarization unit vectors of the beams are defined as $e_i$ and $e_f$. We can easily know the transfer energy $\hbar \omega$ and the transferred momentum Q equal to the difference between the incident and scattered beam

$$\hbar \omega = E_i - E_f$$  \hspace{1cm} (4.1)
As we defined the scattered angle $2\theta$, the quantity of the momentum transfer can be characterized as

$$Q = 2k \sin \theta$$  \hspace{1cm} (4.3)

Figure 5

A simple diagram shows a universal scattering process. The energy of the incident beam $I_i$ and scattering beam $I_f$ are defined as $E_i$ and $E_f$, the momenta defined as $k_i$ and $k_f$, and the polarization unit vectors are defined as $e_i$ and $e_f$. The momentum transfer of the sample is defined as $Q$, the solid angle is $d\Omega$.

In a scattering experiment we need to observe the scattered intensity, usually the double differential cross section $\frac{d^2\sigma}{d\Omega d\omega_f}$ is measured, which is proportional to it.
The cross section means the count rate of the scattered particles compared with the incident beam. The solid angle \( d\Omega \) and the scattered frequency range \( d\omega \), can affect the cross section.

4.2 Dynamical structure factor

In a photon-electron system, the double differential cross section uses an approximation from Van Hove [26]. The condition is that the incident photon energy is far away from the x-ray absorption edge, and the non-resonant scattering mainly contributes to the scattering. Then double differential cross section can be divided into two terms, Thomson scattering cross section \( \left( \frac{d\sigma}{d\Omega} \right)_0 \) and the scattering function \( S(Q, \omega) \)

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left( \frac{d\sigma}{d\Omega} \right)_0 \cdot S(Q, \omega) \quad (4.4)
\]

\[
\left( \frac{d\sigma}{d\Omega} \right)_0 = r_0^2 \cdot (e_i \cdot e_f)^2 \left( \frac{\omega_f}{\omega_i} \right) \quad (4.5)
\]

where the initial and final frequency are \( \omega_i \) and \( \omega_f \), and \( r_0 \) is the classical electron radius

\[
r_0 = \frac{e^2}{m_e c^2} \quad (4.6)
\]
It is easily to know the order of the radius is around $10^{-26} \text{cm}^2$. If the transferred energy is small when compared with the incident energy, the ratio of the frequencies nearly equals to 1.

For a many-electron system, we can assume the electrons’ positions are $r_j$ and the initial and final states are $\Psi_i$ and $\Psi_f$, and the electromagnetic wave is $e^{iQr}$, the scattering function can be presented as

$$S(Q,\omega) = \sum_{i,j} \left| \langle \Psi_f | \sum_j e^{iQr_j} | \Psi_i \rangle \right|^2 \cdot \delta(\omega - E_f - E_i) \quad (4.7)$$

The delta function exhibits the frequency of the excitations and the probabilities of the excitations in the scattering are included in the sum of the matrices, this function is also called the dynamical structure factor.

$$S(Q,\omega) = \frac{1}{2\pi} \int dt e^{-i\omega t} \left\langle \Psi_f | \sum_{i,j} e^{-iQr_i(t)} e^{-iQr_j(0)} | \Psi_i \right\rangle \quad (4.8)$$

Another representation of the structure factor from Van Hove [37] has a Fourier transformation with the electron density $n(r,t)$, which includes the change of the position with the time $r_j(t)$ in the density correlation function.

$$S(Q,\omega) = \frac{1}{2\pi} \int dr e^{-i\omega t} \int dr' \int dr'' \left\langle n(r',t) n(r'',0) \right\rangle e^{-iQ(r' - r'')} \quad (4.9)$$

There is a distance $r''$ from the start point at time zero and position $r'$ to the new position $r' + r''$ after a period $t$, and the expectation value from the initial to the final state plus the stable state contributes to the structure factor. At this point we
can find the energy $h\omega$ and the momentum $Q$ of the scattered beam, which the parameters to probe the properties of the system in the excited state which we can measure.

A more complicated system with atoms needs to include the atomic information. In the first step, we simplify the problem by dealing with one atom per unit cell in a crystal, and then the position of this atom is $R_i$, $u_i$ is the equilibrium position of this atom, and $v_i(t)$ is the displacement from the origin in the period $t$

$$R_i = u_i + v_i(t)$$ \hspace{1cm} (4.10)

The crystal has $N$ atoms, and the crystal structure factor [38] can be substituted into the formula of the dynamic structure factor

$$F(Q) = N \int dV n(R) e^{-iQr}$$ \hspace{1cm} (4.11)

$$S(Q,\omega) = \frac{|F(Q)|^2}{2\pi} N \int dte^{-i\omega t} \sum_{i,i'} \{\exp(-iQ(u_{i'} + v_i(t))) \exp(iQ(u_i + v_i(0)))\}$$

\hspace{1cm} (4.12)

$$S(Q,\omega) = \frac{|F(Q)|^2}{2\pi} N \sum_{i,i'} \exp(-iQ(u_{i'} - u_i)) \int dte^{-i\omega t} \{\exp(-iQ((v_i(t) - v_i(0)))\}$$

\hspace{1cm} (4.13)

The distance between the two atoms $i'$ and $i^*$ is $u_{i'} - u_i$, and we can assume one of the atom’s position is zero and the amplitude is changed to $e^{-iQu}$. 

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For elastic scattering the expectation value of the excitation amplitude
\[ \langle \exp(-iQ((v_r(t) - v_r(0))) \rangle \]
can be regarded as the Debye Waller factor, which is presented as \( e^{-2W} \) then the dynamical structure factor will show the information of the Bragg scattering.

\[ S(Q, \omega) = N|F(Q)|^2 e^{-2W} \sum_s \exp(iQu_s)\delta(\omega) \quad (4.14) \]

The inelastic scattering shows up as a higher order of the scattering process. Mermin, Wagner, and Hohenberg proved the harmonic approximation with the creation and annihilation operators can provide a method to solve for the intensity in the elastic scattering [39-41], and the displacement of the atom can be expressed with the operators and the amplitude [42]

\[ u_l = \sqrt{\frac{\hbar}{2NM}} \sum_s \frac{e_s}{\omega_s} \left[ a \exp(iqr_l) + a^\dagger \exp(-iqr_l) \right] \quad (4.15) \]

where \( e_s \) is the polarization vector of the phonon and the \( \omega_s \) is the frequency of the phonon, then with the operator we can expand \( \langle \exp(-iQ((v_r(t) - v_r(0))) \rangle \) as a series

\[ \langle \exp(-iQ(v_r(t) - v_r(0))) \rangle = \]

\[ e^{-2W} \left[ 1 + \langle Q \cdot v_r(t) \rangle \langle Q \cdot v_r(0) \rangle + \frac{1}{2} \langle Q \cdot v_r(t) \rangle^2 \langle Q \cdot v_r(0) \rangle^2 + \cdots \right] \quad (4.16) \]

The first order is the Bragg peak and the second order is the single phonon produced by scattering, the higher orders are more complicated and usually are much
smaller than the second one. For the phonon we hope to measured, the intensity of the first order scattering is enough.

By substituting the creation and annihilation operators we can have

\[ \langle Q \cdot v_r(t) \rangle \langle Q \cdot v_r(0) \rangle = \frac{\hbar}{2MN} \sum_s \left| \frac{Q \cdot e_s}{\omega_s} \right|^2 \left[ n \exp(iqr_s - i\omega t) + (n + 1) \exp(-iqr_s + i\omega t) \right] \]  (4.17)

where \( n \) is the occupation number

\[ n = \frac{1}{\exp(\frac{\hbar \omega_s}{k_B T}) - 1} \]  (4.18)

From equation 4.13 and 4.17, we can get the dynamical structure factor for the first order inelastic scattering

\[ S_{\text{1st}}(Q, \omega) = \frac{\hbar}{2M} |F(Q)|^2 \]

\[ \cdot \sum_{i,s} \left| \frac{Q \cdot e_s}{\omega_s} \right|^2 \exp(-iQ\mathbf{a}_s) \left[ n \exp(iq\mathbf{a}_s) \delta(\omega + \omega_s) + (n + 1) \exp(-i\mathbf{a}_s) \delta(\omega - \omega_s) \right] \]  (4.18)

This function describes two opposite processes, the creation and the annihilation of one phonon which have a positive and a negative energy, and if this process occurs in a crystal, the reciprocal lattice vector can determine whether the process can happen. For the system with \( N \) identical atoms, we can calculate most of
the components of the dynamical structure factor by the properties of the specific material and $S(Q,\omega)$ only depends on the frequency and the momentum of the phonon, which we can measure in the experiment or calculate with the DFT implemented by Quantum Espresso.

$$G = Q \pm q$$ (4.19)

$$\sum_i^n \exp(i(q \pm Q)u_i) = N\delta(G \mp q - Q)$$ (4.20)

$$S_{inelastic-scattering}(Q,\omega) = N\frac{h}{2M}|F(Q)|^2 \sum_s \frac{|Q \cdot e_s|^2}{\omega_s} \cdot \Delta(G,\omega_s)$$ (4.21)

$$\Delta(G,\omega_s) = \left\{ \begin{array}{l} n\delta(\omega + \omega_s) \\
(n+1)\delta(\omega - \omega_s) \end{array} \right\} \cdot \delta(G - Q \mp q)$$ (4.22)

For the system with $N$ different atoms, for a specific atom $d$ in the $p^{th}$ phonon branch, all the atoms can contribute to this branch [43]

$$S_p(Q,\omega) = \frac{1}{2\omega_p} \left| \sum_{d,p} \frac{Z_d}{M_d} \exp(iQr) \left[ Q \cdot e_{p_d} \right]^2 \right| \cdot \Delta(Q,\omega_p)$$ (4.23)

where $Z_d$ is the atomic number of the $d$ atom. In the simulation, the phonon frequency and eigenvector of a phonon wavevector can be calculated, and the dispersion and intensity of the phonon can be obtained from the calculation. In the experiment, the phonon energy can be acquired by measuring the cross section.
4.3 Introduction to inelastic x-ray scattering experiments

Inelastic x-ray scattering is a technique developed with the improvement of synchrotron radiation. In the early days, the beam’s brilliance and flux from the first generation synchrotron radiation was limited to a low level, and the energy of x-ray was usually on the order of 10keV. Diffuse x-ray scattering can be utilized to probe the lattice dynamics. Walker executed the first experiment measuring the diffuse x-ray scattering intensity of aluminum in 1956 [44]. However, it was impossible to use inelastic x-ray scattering to measure the phonon dispersion during this period because the energy shift in the process of creating or annihilating a phonon was impossible to detect. The typical inverse frequency of an x-ray (10^{-16}s) from synchrotron radiation is much shorter than the time for the motion of the atoms (10^{-14}s), which means only a temporary configuration can be observed [45]. With the third generation synchrotron radiation sources, inelastic x-ray scattering becomes a feasible technique for measuring the phonon dispersion of the compound due to the increasing intensity and energy resolution. Dorner and Burkel performed the first measurement of phonon dispersion by inelastic x-ray scattering in 1987 [46]. With the further development of the third generation synchrotron sources, and the evolution of the undulators and monochromators, higher energy resolution has been achieved and the inelastic x-ray scattering is widely used in many domains.
X-ray scattering is not the mostly common method to measure the energy transfer from the lattice vibrations and the motion of the atoms. Neutron scattering is the first choice to accomplish this work. The neutron’s wavelength is compatible with the atomic spacing of the lattice. The measured energy and momentum transfer of neutron is restricted because the energy of the neutron is restricted to the momentum for the large energy transfer, which is called the kinematic restriction. Neutrons mainly interact with nuclei and have a strong scattering after entering a magnetic field, which can help us understand the excitation of the elements and the magnetic structure of the matter. Meanwhile, the favorable penetration performance of neutrons can provide an efficient tool to study the internal structure of the bulk materials. Similar to neutron, the wavelength of x-ray is compatible with the atomic spacing, but there is no kinematic restriction or energy transfer restriction. In contrast, although both x-ray and neutron have absorption, the behaviors are different. X-ray has strong absorption if the energy of photons is low, and neutron has strong absorption for some special elements such as Cd, B and Gd. Different from the fact that neutrons interact with nuclei, x-rays principally interact with electrons, which make them a good tool to study the electronic structure. The x-ray source has a much higher brilliance than the neutron source, which can satisfy the requirement for a small sample such as 100 microns, or even smaller. This point is very important for the high-pressure experiments because the sample size should be small enough to be set up inside the
high-pressure device. However, the radiation of x-rays may also damage the sample if the energy is low, and it is not very sensitive for magnetic field and usually has a weak magnetic scattering.

The advantage of x-ray attracts many people to study and improve the scattering technique since 1980s. The new monochromators provide a better incident x-ray beam and the energy resolution is increasing gradually.

4.4 Energy resolution

The relation between the energy and the wave vector of the phonon can be written as

$$\frac{\delta E}{E} = \frac{\delta k}{k} \quad (4.24)$$

where $\delta E$ is the energy resolution and $\delta k$ is the uncertainty of the wave vector that creates the resolution. The resolution comes from two contributions, the scattering geometry contribution and the crystal contribution. The intrinsic quality of the crystal and the order of the reflection mainly affects the crystal contribution, and the scattering geometry and divergence of the beam can affect the geometric contribution.

For the crystal contribution, the best solution to minimize the uncertainty of the crystal contribution is to choose a perfect crystal to avoid strains, distortion or
mosaic. Meanwhile, the reflection of the x-ray beam only happens in the thin surface of the crystal, the uncertainly of the energy from the reflections (multiple scattering) brings an energy distribution. Darwin [47] proposed the solution for the multiple scattering, and James [48], Boris W. Batterman and Henderson Cole [49] performed the further summary of dynamical diffraction theory of x-rays for perfect crystals. The depth of the penetration of an x-ray inside the crystal is also called the extinction depth, and the energy distribution is called the Darwin curve. After the simplification, we have a formula with the depth.

$$\left( \frac{\delta E}{E} \right)_{\text{crystal}} \propto \frac{1}{\tau_{\text{ext}}} \quad (4.25)$$

which shows a good energy resolution requires a long extinction depth. A higher order reflection can extend this length. However, the absorption of x-ray is not included in this process. When the incident beam has a higher energy, the absorption depth is shorter than the extinction depth and the absorption will overwhelm other effects and govern the penetration, instead of the calculated extinction depth.

The penetration depth is defined as the depth where the intensity is reduced to $1/e$ of the initial value. For the energy above $\sim$15keV, the absorption effect begins to dominate the energy resolution and limit the improvement [45], since the penetration depth is proportional to the absorption depth. In the experiments, a Si reflection is the most common choice to achieve high resolution (<10 meV) but the
high order reflection will bring a lower reflectivity [50]. Usually the practical method is a compromise between the reflectivity and resolution.

The geometric contribution has two different cases for the crystals if they are flat or curved, which are corresponding to the monochromator and analyzer in the IXS spectrometer. The modern design monochromator with one crystal has reached a very small value of $\delta E / E$ to satisfy the energy requirement [51] and a very long distance from the sample to distinguish the reflected beam is needed. Meanwhile, the control of the energy by changing the Bragg angle is also limited by the resolution function and space. Tuning the lattice constant of the crystal with the temperature is a reasonable method to control the energy,

$$\frac{\Delta E}{E} = \alpha \Delta T \quad (4.26)$$

with an expansion coefficient $\alpha$, the energy change is easy to find as a function of $\Delta T$. The material of the crystal determines the convenience of tuning the energy, such as silicon with an coefficient $2.56 \times 10^{-6} K^{-1}$ [52] can be cut as a good crystal to set up a monochromator. Meanwhile, the asymmetric channel-cut crystals can also tune the energy by reducing the divergence of the beam [53].

For the analyzer, there are two reasons to use curved crystals [50]: collect the intensity in the larger solid angle for a small range in the detector; and focus onto the detector. The ratio between the source-crystal and focus-crystal distance is called the
demagnification ratio. The resolution will be increased when the ratio approaches one, it means the detector and the source should be close enough for a better resolution.

The design of the analyzer usually chooses the bent crystal. For reducing the bending stress of the crystal in the bending, the crystal is cut into diced pieces with a 1mm x 1mm size [54]. A very high resolution requires a long analyzer arm and the low signal rate requires multiple analyzers. For the spectrometer, the geometric contribution and crystal contribution in the monochromator and analyzer should be all included in the calculation of the resolution. The total energy resolution can be described as the sum of the geometric and crystal contribution from the analyzer and monochromators.

4.5 High energy resolution inelastic x-ray scattering (HERIX) Spectrometer at APS

The famous third generation synchrotron radiation sources all have their own IXS beamlines such as European Synchrotron Radiation Facility (ESRF, France), Super Photon Ring - 8 GeV (SPring-8, Japan), and Advanced Photon Source (APS, USA). High Energy Resolution Inelastic X-ray (HERIX) spectrometer is one of the important components of these facilities. The HERIX spectrometer at APS is located in sector 30. Sector 30 has both HERIX and MERIX (Medium energy resolution inelastic x-ray), which have different monochromators.
The white beam comes from the storage ring and goes into station A. Station A includes a compound refractive lens (CRL) and a high heat load monochromator (HHL). CRL is a group of lens in a linear array to focus the x-ray to at the desired energy from the incident white beam [55]. The HHL is composed of two parallel water-cooled diamond C (111) crystals, which provide a stable beam with small energy deviation (~1.6eV). Station B includes a high-energy-resolution monochromator (HRM) and MERIX spectrometer, and Station C includes bimorph focusing mirrors and HERIX spectrometer. HRM is composed of three pairs of parallel crystals that work at 123 K and the energy bandwidth is 1.1 meV [56]. The beam will go through the high-energy-resolution monochromator and bimorph focusing mirror, and at last reach the HERIX spectrometer.

The bimorph focusing mirror can focus the beam with a size 35 μm x 10 μm (horizontal x vertical) and the analyzer crystal is a Si (12 12 12). The incident x-ray beam has an energy 23.724 keV. The total energy resolution is around 1.5 meV. The maximum momentum transfer is 74nm⁻¹ and the momentum resolution with full analyzer is 0.6nm⁻¹. For collecting the solid angle as large as possible, nine analyzers are arranged in a line at the end of the arms and the maximum value of 2θ is 35 degrees. The CdTe detectors with 3x3x1 mm³ size are mounted on a thermoelectric cooler and the working temperature is around 248K (-25°C).
Figure 6

Schematic of the HERIX Spectrometer in Sector 30 at Advanced Photon Source (APS), Argonne National Laboratory (ANL).

Figure 7

Bimorph focusing mirror before the sample in the HERIX station.
The HERIX arms and the CdTe detector in the HERIX station.

A closed cycle cooling system with a base temperature of ~4 K and the ruby fluorescence system for measuring the pressure of high-pressure samples can be easily integrated into the beamline. These are used to obtain low temperatures and a pressure-measurable environment in our experiments.
CHAPTER V

HIGH PRESSURE TECHNIQUE

5.1 Diamond anvil cell (DAC)

The diamond anvil cell (DAC) is a device used to supply the high-pressure environment in the experiment. DAC usually exerts pressure on a small sample, and because the diamond surface is small (on the order of 100 microns), the pressure can be up to 300GPa [57]. This device can be used to simulate the inner environment of the planets, and study the properties in the materials under extreme conditions.

The DAC is composed of two diamonds, and the sample is between the opposed culets. Diamond can guarantee the force is correctly exerted without deformation, but it needs a pressure medium to supply a stable hydrostatic force on the sample to avoid damage, misposition, uniaxial and microscopic stress that would result from direct contact [58]. The pressure medium can be helium, neon, silicon oil, argon, hydrogen, mixed methanol–ethanol or some soft solid [59]. Most media can be used at low pressure and they have their appropriate range [60]. Meanwhile, because directly measuring a pressure is very hard in the small space of a cell, a pressure standard is chosen to measure indirectly. Some suitable material are ruby, silver, and
gold. As a reference, the ruby fluorescence [61] at different pressure has been measured and fit to a function.

Figure 9

Simple schematic of Diamond anvil cell (DAC), the sample and pressure standard are enclosed inside a drilled hole in the gasket by the two diamonds and the gasket, and the pressure medium ensures the force exerted on the sample and standard is a hydrostatic force. The direction of the incident and scattered beams are limited by the diameter of the radial port of the cell.

H. K. Mao considered the calibration curve of the pressure shift of the ruby emission line in 1986 [62] and on the basis of this work, online and offline ruby fluorescence systems are easy to set up and connected with the visual pressure-measuring program, which is an important component in the high pressure experiment. The material of the gasket between the diamonds can be stainless steel.
301, beryllium, rhenium, or tungsten, the first and second are usually used in the x-ray experiments.

Figure 10
a) A symmetric piston-cylinder DAC When the pressure is increased, it is important to keep the exerted force along the axis of the centers of the diamonds. The beveled washers provide elasticity as springs. b) A short symmetric piston-cylinder cell mounted into the holder with the membrane covering instead of bolts. By charging the gas with the gas tube, the membrane can tune the pressure inside the cell.

5.2 Preparing the cell

The diamond anvil cell used in the inelastic x-ray scattering usually is a Mao-type symmetric cell or short symmetric cell. The former one has a larger height, but the internal structures are the same. The larger height also means a thicker holder, which means the size of the holder with membrane should be considered before mounting if a cooling system is used.

For preparing a cell, the first step is fixing the diamonds on the diamond seats. The material of the seat is WC (tungsten carbide). The seats and diamonds are cleaned with Ethyl alcohol in a small vessel on the ultrasonic machine. Checking the surface of diamonds and seats is necessary before and after the cleaning because any remaining glue or other dirt may seriously affect the observing. The checking of the quality of the diamond is also important, if it is broken or cracked, a high pressure may lead to a fragmentation. When there is nothing on the surface, we can begin to align the diamonds and the seats.
The alignment needs to make the centers of the diamonds and seats coincide. Firstly, the seat is required to be fixed on the bottom of the holder and not slide. The back of the seat is close to the bottom. When the diamond is put on the face of the seat, the top part of the holder keeps it down. The center of the diamond should coincide with the center of the seat by repositioning the seat with the screws. Because this step requires high accuracy, all the work is done under the microscope. Alignment of the centers of the diamonds and seats by the microscopic requires patience and care, and the iterative checking runs through the ensemble procedure.

After the alignment, the work is to affix the diamonds to the seats with the glue. The glue is a mixture of Stycast 2850 FT Black Epoxy and Catalyst 23 LV. The mixing ratio between the Epoxy and catalyst is 100:7.5 by weight. Sticking the diamonds requires one ensure the glue is symmetric around the diamonds to avoid the unbalance. After gluing, rechecking the alignment of the centers is also indispensable. Misplacement will result in the beam being unable to go through the diamond, and one needs to cut off the glue and repeats the cleaning and alignment steps.
Figure 11

a) The back and face of a diamond seat. b) Fixing a diamond on the face of a seat and aligning the centers. c) Gluing the diamond on the seat and checking the alignment.
5.3 Loading the sample

The gasket is created after we have finished the preparation of a DAC. The thickness of the drilling hole depends on the thickness of the sample and the loading gas. The gasket will be compressed by turning the screws and a crater is produced when it is set up in the cell between the diamonds and sits on the wax. Marking on the gasket is necessary for resetting. Both laser and mechanical means can drill a hole inside the crater, but the laser drilling has a better quality. The laser micro-drilling system in Sector 13 at APS provides a quick and convenient way to accomplish this work. This system contains a 100-watt fiber laser which is produced by Newport Corporation. The laser spot is about 5 microns, and every laser scan can drill a thickness about 10~15 microns. This system is a part of the GSECARS laser laboratory.

The sample loading can start after every step of assembling the cell is finished and the alignment is considered perfect. The diameter of the top face is usually from 800 to 300 microns, and the diameter of the hole is half or one third of this. Moving the sample and ruby (or other standard) to the center of the face by hand or motor demands skill, tricks and patience, because the size of the sample may smaller than 100 microns (and the ruby ball used as pressure standard is around 10 microns).
Although in some conditions the membrane can tune the pressure in situ, the gas loading before the experiments is also a choice. The pressure would be around 1GPa after closing the cell. The gas loading system in Sector 13 at APS can charge with helium, neon or hydrogen. The system uses motor driven screws to close a clamping device, so it does not need to tighten the screws directly because this device clamps the DAC [63]. At the same time, this system also uses the ruby fluorescence to measure the pressure, and a failed sample loading can also be identified before the charging. After the gas loading, turning the screws and checking the internal pressure of DAC with the offline ruby-fluorescence system gradually can help us approach the target pressure. A slight tightening of the screws in the high-pressure range can result in a sharp pressure increase. It requires reducing the size of the turning iteration to one-step of 30 or 15 degrees to avoid the large pressure increase.

In our experiment, the gasket is made of stainless steel 301 and the diameter of the diamond cutlet is 500 microns. Because helium may shrink very seriously in the cryogenic experiment (even >50%), it is unsuitable to measure good data, so neon is chosen as the pressure medium. Although a gas, neon will liquefy and solidify under pressure, so the shrinkage level is acceptable. The pressure standard is a ruby ball (5~10 microns, better but more expensive than the ruby crystal). Although cleaning in every step is indispensable, it is possible for dirt to remain inside the hole. A big
separation between the sample and the gasket hole can provide a good transparent space for x-rays.

Figure 12

The clamp device of the gas loading system in Sector 13 at APS.
Figure 13

A chromium single crystal inside the DAC after gas loading. Most of remnants come from the condensed gas loading.
CHAPTER VI

EXPERIMENTAL DETAILS

6.1 Measurements

The phonon dispersion relation of chromium was measured at room temperature (297 K), and 5K by IXS. At room temperature, we chose three pressure points: 1.29 GPa, 8.15 GPa and 10.6 GPa. At 5 K, we measured one pressure point at 18.36 GPa.

Figure 14
The measured points in the phase diagram, the yellow region is the quantum critical regime and the green region is classical critical regime.

In the high pressure environment, the ruby fluorescence needs to be calibrated and the measured value has a shift from the authentic pressure, Feng’s paper [12] implied a linear relation of the crystal constant and shifted pressure from 0 to 20 GPa, and the shifted pressure is around 1.5 GPa in our measurement. However, the real pressure in the cooling process may be affected for many reasons. The shrinkage of the cell and gasket will change the internal pressure in the pressure medium, and also results in that the pressures in the different positions such as the center of sample and ruby have a large difference. The ruby fluorescence at low temperature has a different behavior from room temperature, which requires a calibration to the relation between the wavelength of the fluorescence and the pressure. Meanwhile, the calibration at high pressure usually depends on the empirical formula, which requires verification by experiment before applying.

The pressure of the sample is measured by the online ruby fluorescence system in Sector 30, and the temperature is tuned by a new designed displex cryostat compatible with the holder’s size. The size of the single crystal chromium sample is 125 x 50 x 30 μm3, which is cut from a high-purity single crystal wafer oriented along (100) direction, and polished by an electrochemical machining (ECM).
Because the size of the symmetric cell is not suitable for the membrane, the pressure in the cell is increased by tightening the screws steeply and smoothly.
b)
6.2 The inelastic x-ray scattering data

There are nine analyzers at the end of the arm in the HERIX. When the longitudinal phonon branch is measured, the scattered beam from the center analyzer
(analyzer 5) will contain the phonon peak of the input momentum value, and the scattered beam from the neighboring analyzers with equal separations measure the phonon peak with the equally spaced momentum from the input value. When the transverse phonon branch is measured, only the beam from the center analyzer shows the phonon peak. Because all the analyzers are in the horizontal plane, the beam from the other analyzers can not measure a phonon dispersion along the transverse direction. The inelastic neutron scattering indicates that there is a phonon softening close to the boundary along the direction (1 0 0) at room temperature [64]. The two transverse modes have the same behavior, while the longitudinal mode is clearly different. Meanwhile, high-pressure will compress the lattice constant of chromium and affect the phonon's behavior, which is obvious in the longitudinal branch. For comparing the phonon dispersion efficiently in the different states, we choose to measure the phonon along the direction (1 0 0). In the odd Brillouin zones, the diffraction peak is forbidden and so there is little intensity. For a better intensity, (2 0 0) is the actual measured direction. In the experiment, three Q-sets have been measured, (2.9 0 0) at room temperature, (2.5 0 0) & (2.82 0 0) at 5 K. Because some analyzers are out of the range and bad data exists for many unpredictable reasons such as the intrinsic quality of the crystal sample or slight misalignment from the center of the beam, the data sets do not include all the analyzers in the range.
<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>analyzer #</td>
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<td>( K )</td>
<td>( L )</td>
<td>in the range</td>
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<td>0.02</td>
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<td>-0.01</td>
<td>*</td>
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<tr>
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<td>-0.01</td>
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<tr>
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<td>-0.02</td>
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<tr>
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<td></td>
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<tr>
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<td>( K )</td>
<td>( L )</td>
<td>in the range</td>
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<td>0.02</td>
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<td>2.85</td>
<td>0.09</td>
<td>-0.03</td>
<td>*</td>
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Table 3

The positions of analyzers 1-9 when (H K L) is (2.82 0 0)

<table>
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<th>K</th>
<th>L</th>
<th>in the range</th>
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<td>-0.06</td>
<td>0.02</td>
<td>*</td>
</tr>
<tr>
<td>analyzer 3</td>
<td>2.65</td>
<td>-0.04</td>
<td>0.01</td>
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<td>2.73</td>
<td>-0.02</td>
<td>0.01</td>
<td>*</td>
</tr>
<tr>
<td>analyzer 5</td>
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<td>-3.9E-06</td>
<td>7.2E-07</td>
<td>*</td>
</tr>
<tr>
<td>analyzer 6</td>
<td>2.91</td>
<td>0.02</td>
<td>-0.01</td>
<td>*</td>
</tr>
<tr>
<td>analyzer 7</td>
<td>2.99</td>
<td>0.05</td>
<td>-0.02</td>
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</tr>
<tr>
<td>analyzer 8</td>
<td>3.08</td>
<td>0.07</td>
<td>-0.02</td>
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<tr>
<td>analyzer 9</td>
<td>3.16</td>
<td>0.1</td>
<td>-0.03</td>
<td></td>
</tr>
</tbody>
</table>

In the cryogenic and high-pressure environment, the counts into the detector can be reduced to half or one third of the counts at room temperature and atmosphere. Although the reduced excitations in the cryogenic environment also result in the reduced background, the phonon peak may be difficult to identify from the background noise if the cell and alignment is not perfect. Repeating scans to reduce the error is necessary for a reasonable data set, usually three or four times. Meanwhile, the scanning time of IXS requires much beam time, so it is hard to measure the phonon points as desired. However, the change of the phonon dispersion and phonon anomaly in chromium can be studied in some specific
range, such as from (0.9 0 0) to (1 0 0) or around (0.5 0.5 0). In our experiment, we focus on the change of the phonon anomaly near the H point (1 0 0), which can help us understand the phase transition.

![The longitudinal branch at 18.36 GPa and 5 K $Q = (2.5 0 0)$](image)

Figure 16

There are two peaks in a scan set, the elastic peak at zero energy loss and the phonon peak with the phonon energy at a specific phonon wave vector.
The IXS data in the longitudinal phonon mode for Cr at 1.29 GPa and 297 K. The scan time of every point is 120 seconds. $Q = (2.5\ 0\ 0)$ at analyzer 5.
Figure 18

The IXS data in the longitudinal phonon mode for Cr at 1.29 GPa and 297 K. The scan time of every point is 90 seconds. $Q = (2.9 \, 0 \, 0)$ at analyzer 5.
The IXS data in the longitudinal phonon mode for Cr at 8.15 GPa and 297 K. The scan time of every point is 120 seconds. $Q= (2.5 \ 0 \ 0)$ at analyzer 5.
The IXS data in the longitudinal phonon mode for Cr at 8.15 GPa and 297 K. The scan time of every point is 90 seconds. Q = (2.9 0 0) at analyzer 5.
Figure 21

The IXS data in the longitudinal phonon mode for Cr at 10.6 GPa and 297 K. The scan time of every point is 120 seconds. $Q = (2.5 \ 0 \ 0)$ at analyzer 5.
The IXS data in the longitudinal phonon mode for Cr at 10.6 GPa and 297 K. The scan time of every point is 90 seconds. $Q = (2.9 \ 0 \ 0)$ at analyzer 5.
The IXS data in the longitudinal phonon mode for Cr at 18.36 GPa and 5 K. The scan time of every point is 120 seconds. $Q = (2.5 \ 0 \ 0)$ at analyzer 5.
Figure 24

The IXS data in the longitudinal phonon mode for Cr at 18.36 GPa and 5 K. Q = (2.82 0 0) at analyzer 5. The scan time of every point is 120 seconds.
The IXS data in the longitudinal phonon mode for Cr at 1.29 GPa and 297 K. The scan time of every point is 120 seconds.
The IXS data in the longitudinal phonon mode for Cr at 8.15 GPa and 297 K. The scan time of every point is 120 seconds.
The IXS data in the longitudinal phonon mode for Cr at 10.6 GPa and 297 K. The scan time of every point is 120 seconds.
6.3 Data analysis

The elastic and inelastic peaks in the longitudinal branch are fitted together. The fitting functions are Lorentz functions because they fit the sharp peak well. Every data set at room temperature is made up of two scans, one scan is around the elastic peak, and another is around the phonon peak. After interpolating, the elastic peak is set to be at the zero position, and then the phonon energy is the distance from the phonon peak to the elastic peak. Double-peak fitting ensures the combined scan perform uniformly and reduces the total scanning time.

Some phonon peaks in the longitudinal mode from the specific directions are weak, and the reason for the weakness may come from bad crystal quality, imperfect reflection from analyzers or very small misplacement during the aligning. Some particular momenta have weak signals and their phonon peaks have broad widths, which shows the sample is not very perfect and the mosaic may be changed in the experiment. However, most of the phonons can be measured and their values are in the expected range, and the fitting ensures the phonon can be considered and not covered up by the background.

When the pressure increases at room temperature, the phonon energy along both the longitudinal branch and transverse branches also increases. At low temperature, the counts are reduced to half or one third. At the same time, the noise is
also reduced with the same level or more, which helps us distinguish the weak phonon from the noise. The data set (2.82 0 0) provides three useful phonons, the first two phonon energies can be validated by the former data set, and the palpable peak in analyzer 6 around (2.9 0 0) is substantially accurate. All the scans at 5 K also show the phonon energy is higher than the room temperature, and the details will be compared with the simulation result next chapter to discriminate from the phonon dispersion at room temperature.

The phonons in the transverse modes are measured at both room and low temperatures, but the peaks in the scans at 5K are very weak and hard to fit, which are not included in the figures. The phonon at room temperature shows the phonon near the H point does not change too much, the phonons of 8.15 GPa and 10.6 GPa only have a small difference. The reason is that the lattice constant does not change too much in the compression from 8.15GPa to 10.6GPa, and the transverse branch in this range (0.8 ~1 0 0) has a smooth curve.

The deficiency in the transverse modes at 5K means that it is impossible to find a change of the phonon softening at low temperature by comparing the phonons close to the H point. However, the longitudinal phonon showed different behaviors
Figure 28

The special points of the bcc structure in reciprocal space. \( \Gamma (0 \ 0 \ 0) \) H \( (1 \ 0 \ 0) \) N \( (1 \ 1 \ 0) \) P \( (1 \ 1 \ 1) \).

6.4 The lattice constants at different pressures

The lattice constant can be measured with x-rays, using Bragg's Law, when the incident energy of the beam and the scattering angle is known, the distance between the two atomic layers is easy to solve. In sector 30, the lattice constant can be directly acquired in the measurement. The lattice constant of a bcc-structure unit cell in chromium is 2.884 Å at atmosphere pressure, and is reduced with increasing pressure. However, at low temperature, the material shrinks due to the thermal
contraction. The pressure standard is also affected by the temperature. The online ruby fluorescence system can calibrate the fluorescence peak line's position with the temperature.

![The lattice constant of chromium at 297 K](image)

**Figure 29**

The lattice constants in Cr at room temperature. The red line is the fitting line.

When all the pressure points except 5 K and 18.36 GPa are fitted, the linear relation of the pressure and the lattice constant is implied, which shows the structure in only rigidly suppressed without transformation at room temperature. However, at low temperature, the measured lattice constant (2.81746 Å) is far from the fitting line. The pressure change cannot be estimated as the relation at room temperature.
6.5 The phonon dispersion and Fermi surface

The phonon dispersion curve can be plotted with the measured phonon energy at different Q points. At room temperature, the phonon dispersion in the longitudinal branch of three pressure points exhibits a similar behavior, which proves the pressure does not result in a phonon dispersion curve anomaly at room temperature. The phonon dispersion in the transverse branch shows softening near the H point (1 0 0), which is an anomalous behavior from the normal smooth curve. The reason of this anomaly will be discussed in a later chapter.

![Longitudinal mode for Cr at 297K](image)
The measured phonon dispersion in chromium at room temperature and different pressure points a) Longitudinal branch b) Transverse branch.

The phonon dispersion in the longitudinal branch at 5K and 18.36GPa with (2.5 0 0) and (2.82 0 0) data set is fitted by a Lorentzian function and the phonon energies are higher than the date at room temperature. The curve at room temperature close to the H point is smooth and gentle. However, the phonon curve at 5K shows that it drops faster than the phonon curve at room temperature. The curve is concave and changes dramatically.
The measured phonon dispersion in the longitudinal mode for Cr at 5 K and 18.36 GPa.

The phonon width can be obtained when the phonon peak is fit. From the uncertainty principle, we know that short lifetime particles have significant energy uncertainty in the measurement. The measured phonon width is affected by the finite size of the analyzer and the instrumental resolution from the spectrometer. The effect of the analyzer size is determined by the diameter of the analyzer and the distance from the analyzer to the sample. The instrumental resolution is 1.5 meV and the measured phonon width should be larger than this value. The phonon peak is not a

Figure 31
delta function and distributed in an energy range. The half-maximum of this distribution is the phonon width. The real phonon width is obtained by reducing the instrumental resolution and the analyzer size’s effect from the fitted result. The square of the fitted width equals the sum of the above three terms’ squares.

Figure 32

The phonon width for Cr at different pressure and temperature.

The phonon widths around (2.5 0 0) are close to the average widths, which are mainly due to the analyzer’s finite size. The phonon widths near the boundary (Γ and H point) are obviously higher than the phonon widths around the center between the
two special points. This is significant because the effect due to the analyzer size is small and the real phonon determines the behavior. The maximum value appears close to the H point. The phonon width at room temperature does not change too much except the range after the point (2.8 0 0), which changes substantially with pressure. The phonon width at 5 K has a similar behavior and larger difference from the average widths.
7.1 The simulation of paramagnetism, antiferromagnetism and SDW

As a standard bcc-structure material, the simplest simulation in chromium only needs to consider the lattice constant and type of Bravais lattice. The non-spin case only has a single kind of atom in the unit cell without spin, which shows paramagnetism above Néel temperature 311K [20].

The AFM case requires that the two atoms in this unit cell have opposite spin directions. However, the software QE only recognizes one type of atom in the bcc structure and it is unable to describe the bcc structure in a super cell with 2x2x2 unit cells. A convenient idea is construct a simple cubic with one center atom, and the corner atom and center atom have opposite spin directions. If the cubic cannot contain a center atom, a super cell with 2x2x2 unit simple cubic cell can also introduce the opposite spins. Although it is a simple idea, it is problematic that sc and bcc unit cells have completely different first Brillouin zones in reciprocal space, and the simulation is based on the k-points distributed in the k-space. The super cell also cannot change the Brillouin zone. Instead, a trigonal structure can be used in the place of the bcc
structure. The trigonal angle is keeping at 109.28 degree, and the lattice constant is \(\sqrt{3}/2\) times the cubic lattice constant. Because there is only one atom in a trigonal unit cell, a super cell with eight atoms is constructed, and the four layers in the cell have a positive-negative-positive-negative spin structure.

![Figure 33](image)

A simple spin-density-wave SDW model. The direction includes spin down, spin up and zero.

Based on the AFM structure, a SDW requires the spins along the specific directions become a chain and the directions change periodically in a plane, as in Figure 2, and then the opposite spins still exist. The length of SDW is 14 times or 28 times lattice constant [20]. It is very difficult to construct a super cell with the real structure; the simulation of a cell containing 14\(^3\) atoms cannot be achieved with current computers. The simplified model of a SDW only requires 2x2x2 or 4x4x4 unit
cells (3x3x3 unit cells include 27 atoms, it is obvious the total magnetism is not zero in the AFM structure). The smallest super cell 2x2x2 can have a simplest chain: positive-zero-negative-zero. For discriminating an AFM structure with and without SDW, relaxing the structure is a feasible method. After the relaxing, the trigonal angle of the AFM structure with SDW is still 109.28 degree, and the structure with SDW may have a small deviation. The change of the trigonal angle denotes the break of the bcc structure. The stability of the AFM structure with SDW comes from the long-range effect of SDW.

The convergence of the self-consistent calculation of every case is tested separately because the total force and stress must be minimized for stability with the different structures. The main variable is the energy cutoff, and the k-points are the same because the different space distribution in reciprocal space can result in a very large change of the phonon dispersion for different structures.

7.2 The simulation result of the phonon dispersion

The simulation of the phonon dispersion at room temperature and ambient pressure shows the phonon in the direction (q 0 0) has two of the same transverse branches. These two branches are separated in the (q q 0) direction as T1 and T2. The k-points grid is 8x8x8 and the lattice constant is 2.884 Å in this case. The simulation shows a paramagnetic structure, no spin is involved.
Figure 34

The phonon dispersion in the paramagnetic state at 297 K and atmosphere pressure.

The simulation of spin-density-wave and antiferromagnetic structure is calculated at all the different pressures. Because the lattice constant is inversely proportional to the reciprocal vector in the cubic structure, the k-points in these two cases are 4x4x4. At 5 K and 18.36 GPa, the lattice constant is 2.81746 Å.
The phonon dispersion in chromium, the lattice constant is 2.81746 Å
L=Longitudinal T=Transverse.

The relaxation of the two structures shows the trigonal angle in SDW does not change, and the angle in AFM has a 0.1-degree deviation: it changes from 109.28 degrees to 109.39 degrees. The comparison of the structures shows a similar curve in the longitudinal branch and their transverse branches are nearly the same. The higher phonon energy in the SDW implies the AFM structure with SDW is more stable even at much high pressure.
7.3 Experimental data and simulation comparison

The phonon dispersion at ambient pressure was first measured by inelastic neutron scattering two decades ago [63]. The softening occurs in the transverse branch around the H point (100) and the N point (0.5 0.5 0). However, when we try to find the difference between the simulation and experimental data, it is convenient to compare the longitudinal branches that can have more points in the measurement.

The comparison of the phonon in the longitudinal branches between the simulation result and experimental data shows that the phonon dispersion deviates from the ideal phonon dispersion with SDW at room temperature. The data at 1.29 GPa fits the phonon curve with SDW better than the data at 8.15 GPa and 10.6 GPa. The lattice constant is 2.876 Å, 2.844 Å, and 2.832 Å corresponding to pressure 1.29 GPa, 8.15 GPa, and 10.6 GPa. The phonon energy in the paramagnetic state is much lower than the phonon energy in the antiferromagnetic state. However, the experimental data shows that the behavior at 5 K and 18.36 GPa is different from the simulation of the paramagnetic and AFM state.

At 1.29 GPa, classical criticality can affect the phonon’s behavior. The data from the maximum value to the H point can fit the simulation curve roughly. The data close to (1 0 0) is a little bit away from the simulation of the SDW. At 8.15 GPa and 10.6 GPa, classical criticality has a smaller affect on the phonon behavior. These data
points are further away from the simulation curve between the maximum values and the boundary. However, the data points with error bars are still roughly in the range of the AFM stimulation, which implies that the temperature mainly dominates the phase transition at room temperature. Pressure does not have the same effect as temperature in this condition.

![The phonon dispersion for Cr at 297 K and 1.29 GPa](image)

**a)**
The phonon dispersion for Cr at 297 K and 8.15 GPa

The phonon dispersion for Cr at 297 K and 10.6 GPa

b) 
c)
Figure 36

The comparison between the simulation results and experimental data at room temperature for three different pressure points. The lines are the simulation of different structure. The circle with error bar is the data. a) 297 K and 1.29 GPa b) 297 K and 8.15 GPa c) 297 K and 10.6 GPa.

There are some other experiments about the quantum phase transition in chromium, which shows that the transition may change the SDW. The wave vector of the SDW alternates with lowering the temperature since the variation of the Fermi surface is only dependent on the temperature [14]. Meanwhile, the quantum phase transition occurring at the critical point is achieved by tuning the pressure, and the inverse Hall coefficient measurement under these conditions show a rapid rise in a narrow transition range and indicate a stable state is taking shape [15]. The fierce variation implies the breaking of the stable magnetic ordering including SDW.

Because the point at 5 K and 18.36 GPa is after the quantum phase transition, the further simulation is executed to find a new structure that can be compatible with the data. The first idea is that the spin flip [65] at low temperature may affect the phonon. However, the phenomena only changed the SDW direction from the transverse direction to the longitudinal direction in the transition, and the AFM still dominates the phonon’s behavior. Breaking the magnetic balance in the unit cell is another method to cast off the effect of AFM, and a model with different numbers of
atoms is tested: 2 in 8 atoms have the positive direction and others have the negative direction. However, this state is not a stable state and the total spin is not zero. If we consider that the atoms with opposite spins cancel out each other, the structure will become a ferromagnetic structure. Although this structure is a fake structure, it has an interesting behavior. The maximum value is the same as the value in the AFM state, and the phonon at H point is similar to the paramagnetic state. The normal ferromagnetic state is also simulated and it has a similar phonon curve but is close to the paramagnetic state near the H point.

![Figure 37](image)

The chromium unit cell with a trigonal structure. Blue and red balls are the atoms with opposite spins. a) AFM structure b) Fake ferromagnetic structure.

Meanwhile, the comparison between the simulation and experimental data at 5 K and 18.36 GPa shows that the phonon behavior is different form the other pressure
points. Although the curve shape is similar to the AFM structure around the maximum value, the phonon near the H point is far away from the simulation. The phonon curve is between the AFM state and paramagnetic state. This behavior is a little bit similar to the ferromagnetic state, which shows the magnetic order after the quantum phase transition may be different from the states at room temperature. The ordering could be a complex combination of spins, but not the same as the random order in the paramagnetic state. The fake ferromagnetic state is a reference state and not a real state.

Figure 38

The comparison between simulation and experimental data for Cr at 5 K and 18.36 GPa.
7.4 Phonon anomaly and Fermi surface

In the simulation, the softening in the phonon dispersion near the H point does not show clearly unless the k-points grid is large enough (16x16x16 or more) and the dynamical matrices are calculated as accurately as possible (8x8x8, etc). However, the cost in computer time is very expensive, 10 times more than the former section’s calculation. Meanwhile, the change of the anomaly at different temperatures is conductive to distinguish the structure transformation, but the fluctuation is limited in a small range (0.5~1mev), which means it is required to have a longer scanning time and measure more Q points near the H point or N point.

In the experiment, there are four or five measured Q points in the transverse mode at every pressure point. It is enough to follow the dispersion and compare with the simulation, but hard to describe a complete anomaly behavior. Moreover, the energy resolution (1~1.5meV) means changes in the phonons are easy to miss when the softening is not large enough.

The simulation of the ferromagnetic structure has more than 5meV deviation from the pure AFM structure at the H point in the longitudinal branch, and from (0.9 0 0) to (1 0 0), the difference between the transverse mode and longitudinal mode is usually smaller than 1.5meV. The experimental data lies between the AFM state and the paramagnetic state from (0.5 0 0) to (1 0 0), while some points are close to the
ferromagnetic state. This large deviation in the extreme conditions cannot be explained by the thermal fluctuation as the change at room temperature. Meanwhile, although the formation of the anomaly below the Néel transition is mainly from the SDW, the complete mechanism is still not clear. The change of the anomaly at low temperature is unclear. Consequently, the longitudinal branch in the phonon dispersion can provide more information than the transverse branch. The change in the longitudinal branch can help us discriminate the change of the state.

For examining the effect of the pressure on the structure, a simulation of the Fermi surface is also implemented. The simulation requires enough k-points to describe the details of the surface. After the self-consistent calculation, the band structure calculation with the large k-points grid can provide the eigenvalue. The specific code bands_FS.x can read and regroup those data into a data file, which can be read by a crystalline and molecular structure visualization program XCrySDen [66]. This program can plot 3D Fermi surface.

The simulation with different pressure points shows nearly the same Fermi surface shapes although pressure is increasing and suppressing the lattice constant. The pressure points at 8.15 GPa and 10.6 GPa lies across the critical pressure at 10 GPa. The Fermi energy of the pressure points at 8.15 GPa and 10.6 GPa has a small difference, which is around 1%. The Fermi energy at 18.36 GPa also does not change too much compared to 10.6 GPa. This slight variation shows that the pressure can
change the Fermi surface gradually at room temperature, and there is no sudden
change in this process. It proves that the temperature dominates the phase transition at
room temperature, and the pressure cannot overcome the temperature in this situation.
The simulation of Fermi surface for Cr. a) 1.29 GPa b) 8.15 GPa c) 10.6 GPa d) 18.36 GPa e) electron pocket at 18.36 GPa f) valence pocket at 18.36 GPa. The direction from the center to the corner is (100), and the direction from the center to the side is (110).
CHAPTER VIII

CONJECTURE AND CONCLUSION

8.1 Magnetic order in the phase transitions

The simulation in all the states shows that phonon dispersion curve of the SDW structure is higher than the other states. The pure AFM state has a little bit lower phonon energy, the ferromagnetic state has much lower phonon energy when it is close to the H point, and the paramagnetic state has the lowest phonon energy. It is obvious that the change of the magnetic order affects the phonon energy. In the Néel transition, the spin ordering changes from random to AFM due to thermal fluctuations. When the temperature is lowered, the system also attempts to reduce the total energy. SDW in the AFM structure is also due to this reason. The total energy in the SDW state is lower than the pure AFM state.

However, a quantum phase transition is driven by quantum fluctuation. This driving force is different from thermal fluctuations, and results in different phonon behavior. The experimental data shows that the phonon dispersion curve deviates far away from the simulation of SDW when it approaches the H point. This performance shows that the magnetic order is not the SDW or pure AFM ordering. It is more
similar to the ferromagnetic and paramagnetic ordering, but not exactly the same. Some other experiments also show SDW may disappear after the quantum phase transition [15]. The ordering may be a mixture of different type order, and can be a different order from the AFM, ferromagnetic or the paramagnetic state.

During the transition, the long-range effect presented by SDW is reduced because the spin directions become random, and the main contribution is replaced by a short-range interaction. Meanwhile, the effect of spin directions may be not as important as before. Neighboring atoms could form bounded electron pairs, and the spin ordering may disappear [67].

There is no conclusive evidence the effect of the SDW totally disappears. The special ordering may still exist in an area. However, it is impossible to have a long-range modulation with the random order in a large range. The disappearance of this modulation means the disappearance of SDW.

8.2 The state after quantum phase transitions

There is a mean-field BCS-like exponential ground state in chromium before the QPT happens [15]. This transition state requires that the temperature should be close to zero and the pressure is between zero and 7 GPa. The distance between the two electrons in Cooper pair can be neither too close nor too far away in the BCS
theory. The distance depends on the Coulomb repulsion and electron-phonon interaction [68-71], and is compatible with SDW. Although this ground state can describe well SDW in the low temperature region, it breaks up at the QPT. The structure near zero temperature undergoes a continuous variation as the pressure increases. The AFM order gradually disappears and the asymmetric spin pairs break up when pressure enters the quantum critical regime. The new quantum state after the QPT exhibits a quantum critical behavior and the experiment hints that the phonon behavior of this new state is different from the other states’ behaviors. Because quantum criticality can affect a large temperature region, the quantum state can exist to a relatively high temperature. In this region, although thermal energy is increased, the effect of thermal fluctuation has not overwhelmed the effect of quantum fluctuations.

In the Néel transition, the state changes from the AFM state to the paramagnetic state when thermal energy is increased. In the QPT, it is possible that the increased quantum energy can bring about another paramagnetic state. However, the simulation implies the phonon at 18.36 GPa and 5 K is far away from the paramagnetic state and similar to the behavior of the real ferromagnetic state at some data points. This interesting result suggests us that the ordering in the new state is not completely random and may have some regularity, which is similar to the ferromagnetic state. This new state could be related to a quantum paramagnetic state.
There are some theoretical models to describe quantum paramagnet. After the transition, the valence bond between the neighbor atoms may exceed other interactions when the temperature is close to zero. This bond results in the paired electrons becoming a singlet. When all nearest-neighbor atoms have equal exchange and coupling, the ground state becomes a valence-bond-solid state and the total spin is zero. In the columnar valence-bond-solid state, spin-rotation symmetry exists, but the rotational and translational symmetries in the lattice spontaneously break [72-74]. When there are excitations in the system, some valence bonds between the electron pairs may be not as strong as usual or even break up and their spins may become random. The valence-bond-solid state seems like a crystal of singlets, where all singlets have the same order. However, the order may be random and the entangled valence bond can act like a liquid of singlets. This ground state is called a spin liquids [75]. Spin-rotation and translational symmetries exist in this state. Although the difference between the valence-bond-solid state and spin liquid state shows long-range order may exist in the valence-bond-solid state after the QPT, it is not the same as the SDW because there is no spin in the singlet. It requires further experiments to verify whether the state is a quantum paramagnetic state and how the quantum state after the QPT affects the phonon.
Figure 40

(a) Columnar valence-bond-solid (VBS) state with excitations.  
(b) Spin-liquid (SL) state with excitations.

In conclusion, although the structure of the quantum state after the QPT is not clear, the experimental data hints it may be a different state from the usual states. The
construction and destruction of the long-range effect from SDW in chromium can provide reference for more complicated systems.

8.3 Summary

In this project, the main object was to probe the QPT with IXS technique and simulations. The HERIX spectrometer in Sector 30 (APS, ANL) was used to measure the phonon dispersion in chromium. The pressure points are 1.29 GPa, 8.15 GPa, 10.6 GPa at room temperature and 18.36 GPa at 5 K. Quantum Espresso in Linux and a small computer cluster with two nodes at APS was used to implement the simulation of the bcc structure in chromium with different states.

The measurement of the phonon at room temperature with different pressure points shows the phonon energy is increasing with the pressure, but the phonon behavior is nearly the same. The phonon softening in the transverse branch varies in a small range near the H point (100) and is similar to neutron scattering measurements.

The measurement at 5 K and 18.36 GPa shows the phonon energy in this point is higher than the phonon energy of the points at room temperature, and the behavior is different from the other pressure points. The curve of the longitudinal mode drops rapidly after it reaches the maximum value around (0.6 0 0) and the curve is not as smooth as the phonon curve at room temperature. The simulation of the bcc structure
with the paramagnetic and AFM states shows the difference between the paramagnetic and antiferromagnetic state. The SDW structure is more stable than the pure AFM structure and the phonon energy in this structure is the highest in all the states. The simulation of the ferromagnetic state shows a different behavior from the AFM and paramagnetic states.

The comparison between the experimental data and the simulation of all the state hints the new state is not an AFM state and the ordering of the atoms may have some regularity in a specified range. This regularity could indicate a quantum paramagnetic state exists after the QPT.
REFERENCES


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APPENDIX

SELF-CONSISTENT CALCULATION WITH QUANTUM ESPRESSO
This Quantum Espresso input file performs a self-consistent calculation in chromium. The simulation of the trigonal structure with the AFM state uses a 4x4x4 k-points grid.

/***Self-consistent calculation sample input file***/

&control
calculation='scf',
prefix='cr',
outdir = '/home/output-dir/',
pseudo_dir = '/home/pseudopotential-dir/',
tstress = .true. ,
tprnfor = .true. ,
/

&SYSTEM
ibrav = 5,
celldm(1) = 9.4166,
celldm(4) = -0.33333333333,
nat = 8,
ttyp = 2,
nspin = 2,
starting_magnetization(1)= 0.5 ,
starting_magnetization(2)=0.5,
ecutwfc = 28.5,
ecutrho = 300,
occupations='smearing', smearing='gaussian', de gauss=0.01,
/
&ELECTRONS
    conv_thr = 1.0d-12,
    mixing_beta = 0.2,
/
ATOMIC_SPECIES
Cr1    51.99610  Cr.pbe-sp-van.UPF
Cr2    51.99610  Cr.pbe-sp-van.UPF

ATOMIC_POSITIONS crystal
Cr1 0.000000000  0.000000000  0.000000000
Cr2 0.500000000  0.000000000  0.000000000
Cr2 0.000000000  0.000000000  0.500000000
Cr2 0.000000000  0.500000000  0.000000000
Cr2 0.500000000  0.500000000  0.500000000
Cr1 0.500000000  0.500000000  0.000000000
Cr1 0.500000000  0.000000000  0.500000000
Cr1 0.000000000  0.500000000  0.500000000

K_POINTS automatic
4 4 4 1 1 1