

ELECTRON PARAMAGNETIC RESONANCE OF LITHIUM NIOBATE
HEAVILY DOPED WITH CHROMIUM AND LITHIUM
NIOBATE CODOPED WITH MAGNESIUM AND IRON

by

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of the requirements for the degree

of

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in

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DEDICATION

This thesis is dedicated to my mother, Carolyn Kay Jorgensen. She pushed me when I needed it and was most influential in getting me to finish my bachelor's degree as successfully as I did. This was absolutely necessary for me to continue my studies in graduate school. She is most responsible for giving me the faith and determination I need to continue pursuing my goals.

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VITA

Jonathan David Jorgensen was born in Provo, Utah on December 20, 1983 to David Allen and Carolyn Kay Jorgensen. His family moved often and while growing up he lived in Evanston, Powell, Cody, Casper, and Gillette, Wyoming, Vernal, Utah, and Farmington, New Mexico. The main constants in his life were his family and all the different swimming teams he competed on wherever his family was. In high school, he qualified for the state meet as a freshman, and placed second and fourth his senior year. He also played trumpet for seven years. He graduated from Kelly Walsh High School in Casper, Wyoming in 2002.

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ABSTRACT

In this thesis, electron paramagnetic resonance (EPR) was utilized in measuring and characterizing the dopant ions in three samples of lithium niobate (LiNbO_3). The first sample was LiNbO_3 of congruent composition doped with 0.25% mol chromium ($\text{LiNbO}_3\text{:Cr}$). This sample was studied in detail using two microwave frequencies, 9.4 GHz and 34.4 GHz. It was also studied both at room temperature and at 10 K. Several centers including complexes of Cr-Cr pairs were observed in addition to the most prevalent axial Cr^{3+} center. The other two samples were $\text{LiNbO}_3\text{:Mg:Fe}$, one of congruent composition and the other of stoichiometric composition. The congruent composition contained 6% mol Mg and 0.02% mol Fe, while the stoichiometric sample contained 0.45% mol Mg and 0.01% mol Fe. The stoichiometric composition contains all the same centers observed in the congruent material, plus two additional centers. Since the stoichiometric material provides EPR spectra of much higher resolution, those centers existing in both compositions were characterized more accurately from the stoichiometric material. A discussion of models for dopant center symmetries, dopant positions in the LiNbO_3 lattice, and the charge compensators required by each center is provided. It is shown that charge compensators play an important role in explaining the existence of the additional centers observed in the stoichiometric material.

INTRODUCTION

In this thesis, electron paramagnetic resonance spectroscopy (EPR) was conducted on three samples of lithium niobate (LiNbO_3). Lithium niobate is widely used in the telecommunications industry for electro-optic and integrated optics, and is also of interest for laser applications.¹ Several topics will be covered in this introduction. The first section of the introduction deals with several important properties of LiNbO_3 , such as the lattice symmetry and how the concentration of intrinsic defects defines the difference between congruent material and stoichiometric material. The second gives an overview of the research which preceded this thesis. The final section explains the basics of EPR, starting with the theory of EPR from a classical perspective, and then from a quantum mechanical approach, and finally a brief overview of the equipment used.

Properties of Lithium Niobate

For this section of the introduction, an overview of the LiNbO_3 lattice and symmetry is given first, and then a comparison between the congruent and stoichiometric compositions is provided with emphasis placed on the importance of intrinsic defects. These intrinsic defects are very important when considering methods for compensating the excess/deficiency of charge introduced by non-isovalent dopants, such as trivalent chromium and iron, and divalent magnesium.

In the ideal stoichiometric composition, LiNbO_3 has two molecules in its unit cell, and this cell has the following dimensions: $a = 5.148$ angstroms, $c = 13.863$ angstroms.

This unit cell is rhombohedral with R3c symmetry. There is no mirror plane symmetry anywhere in the LiNbO₃ unit cell, but there is a glide mirror plane relating the two molecules. This symmetry will only allow point defects with C3 or C1 symmetry. Defects residing on Li or Nb sites will possess C3 symmetry (later referred to as axial symmetry). If a point defect resides on an oxygen site, it will have the lower C1 symmetry (referred to as non-axial symmetry). Oxygen vacancies are extremely rare, and oxygen enters the LiNbO₃ lattice in ideal concentrations, as predicted by stoichiometry. Complex of defects can also have C1 symmetry depending on how the ions are positioned relative to each other.

For most industrial applications, LiNbO₃ is grown in congruent composition, which possesses a large concentration of intrinsic defects. The most common point defects are vacancies of both Li and Nb.² The most prevalent defect is the Li vacancy. Congruent LiNbO₃ is characterized by a Li deficiency,

$$\frac{[\text{Li}]}{[\text{Li}]+[\text{Nb}]} = 48.4\%, \quad (1)$$

from which it can be inferred that for each Nb ion which does enter the crystal, there will only be 0.938 Li ions entering the crystal.³ This is sometimes referred to as a 6% lithium deficiency.

Another common defect is Nb ions occupying Li sites, known as Nb anti-sites (Nb_{Li}). These defects can absorb photons of light energy and be recharged to another valence state. This causes changes in the materials' indices of refraction. This is usually an unwanted effect, and is known as optical damage.

These are the main point defects commonly occurring in undoped LiNbO₃, and all

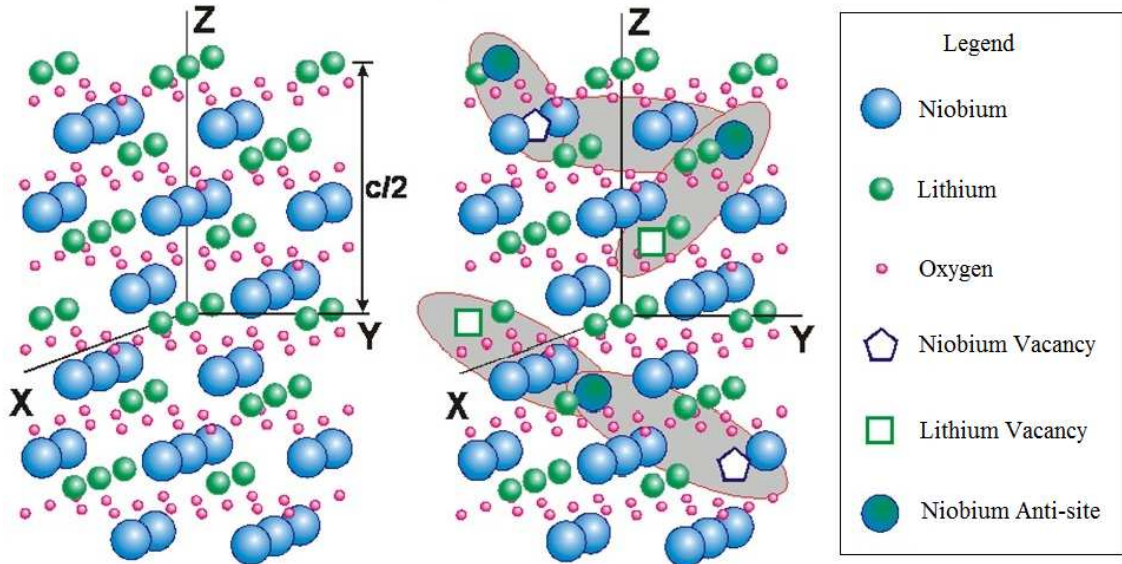
the various defects can act as charge compensators for non-isovalent dopants. The abundance of defects makes congruent LiNbO_3 very tolerant of high concentrations of divalent and trivalent dopants, such as Mg^{2+} , Cr^{3+} , and Fe^{3+} . These dopants most often substitute for Li^{1+} ($\text{Me}_{\text{Li}}^{2+}$ and $\text{Me}_{\text{Li}}^{3+}$), however they can also substitute for Nb^{5+} ($\text{Me}_{\text{Nb}}^{2+}$ and $\text{Me}_{\text{Nb}}^{3+}$) in cases where the material is highly doped. These dopants require charge compensators. It should be expected that the charge compensation mechanism will be different depending on whether the dopant ion occupies a Nb or Li site.

In the congruent composition, there are enough lithium vacancies to compensate all the excess charge introduced by divalent and trivalent dopants occupying lithium sites, so explaining the charge compensation mechanism for a given center is usually not a challenge.

However, in stoichiometric samples, the ideal lattice does not provide the point defects to act as charge compensators, and stoichiometric material is much less accepting of high dopant concentrations. There are even cases when a non-isovalent dopant will not enter the material at all. If the dopant does enter the material, the ions will often introduce point defects in their nearest neighborhood to create new centers not seen in the congruent material. Figure 1 below illustrates the LiNbO_3 lattice. Articles have been published further comparing the properties of the two materials.⁴

The differences between congruent and stoichiometric compositions become even more apparent when considering a codoped crystal, as with the two samples of $\text{LiNbO}_3\text{:Mg:Fe}$ studied in this thesis. Consider the goal of doping a crystal with one element which adds a desired property (active dopant A) and a second which suppresses

Figure 1 – Lithium Niobate Lattice



The figure above compares the ideal stoichiometric lattice on the left with the more common congruent lattice on the right showing some of the most common intrinsic point defects.

an undesired property (modifier M). In the congruent composition, both elements would enter the crystal independently of each other, with no difficulty finding the required charge compensator(s), up to some extreme limit.

This isn't possible in stoichiometric material. The dopants may be more likely to form self compensating complexes, such as $A_{Li} + M_{Nb}$ or $A_{Nb} + M_{Li}$, meaning that the concentrations entering the crystal are now correlated. It is also possible that some complexes will compensate for other centers, i.e. $A_{Li} + A_{Nb}$ compensating some charge for M_{Li} . This can be very important knowledge for applications requiring stoichiometric composition material, since the application might have very specific performance requirements and these dopant complexes can have an impact of the materials' properties. It is understandable then that knowledge of exactly how a given dopant will

find its required charge compensator(s) can be crucial to scientific and industrial growers, since a very nearly stoichiometric crystal can take weeks to grow. Without this knowledge, growers are left to try varying growth parameters, melt concentrations, and possibly post growth reduction/oxidation steps.

Congruent LiNbO_3 is most often grown by the Czochralski method, pulling a boule out of a melt of Li_2CO_3 and Nb_2O_5 . As mentioned before, niobium anti-sites are a common defect of congruent material. These Nb_{Li} sites cause the congruent composition to have a low power tolerance for optical damage, an undesired effect where high irradiance light passing through the crystal causes changes to the crystal's indices of refraction. Thus for optical applications involving high power laser light, stoichiometric material more desirable since it will possess a lower concentration of Nb_{Li} , except that the methods for growing stoichiometric LiNbO_3 are often too expensive. Newer methods for growing stoichiometric LiNbO_3 could possibly address this; however these have yet to see wide use in industry.⁵

There are methods for decreasing the concentration of intrinsic defects of congruent LiNbO_3 , such as using melts with an excess of Li or post-growth vapor transport equilibrium treatment (VTE). Another method for eliminating intrinsic defects is adding potassium (K_2CO_3) into the melt. It is found that potassium does not enter the crystal, and the result will be a crystal with very few intrinsic defects.

The last option is to add an element such as Mg into a congruent composition melt which reduces the number of niobium anti-sites with Mg taking the Li sites itself. This effect occurs strongly once LiNbO_3 is doped with Mg above 4.6% mol, a value

known as the optical damage reduction threshold. There have been studies conducted showing interesting differences between the materials grown with K or Mg in the melt.^{6,7} The congruent sample studied in this thesis was doped above this level, as well as being doped with 0.02% mol Fe. The stoichiometric sample was doped with only 0.45% mol Mg and 0.01% mol Fe, and the smaller concentrations in the stoichiometric media again reflect the lack of charge compensators. Figure 2 below shows the two samples of $\text{LiNbO}_3\text{:Mg:Fe}$, with a 1964 quarter for size reference. Each sample was 4 mm or less on each side.

Figure 2 – $\text{LiNbO}_3\text{:Mg:Fe}$ Samples



The sample on the left was stoichiometric material (0.45% mol Mg and 0.01% mol Fe), while the sample on the right was congruent material (6% mol Mg and 0.02% mol Fe).

The sample of $\text{LiNbO}_3\text{:Cr}$ was congruent material, so achieving the desired dopant concentration did not require any special conditions. However, our research reveals knowledge about defects in the surroundings of certain centers found in heavily doped $\text{LiNbO}_3\text{:Cr}$, as will be further explained later.

Summary of Preceding Research

Iron is always present in LiNbO_3 as a trace impurity from the growth process. It was also researched in LiNbO_3 for its photorefractive properties,^{8,9} thought to be useful for holographic memory devices. For $\text{LiNbO}_3\text{:Mg:Fe}$, it was already well known before this thesis that the most dominant Fe center is $\text{Fe}_{\text{Li}}^{3+}$. When congruent LiNbO_3 is codoped with Mg and Fe, it was also already known that Fe forms at least one new center, but this new center had not been studied in detail before, and that is one of the goals of this thesis.

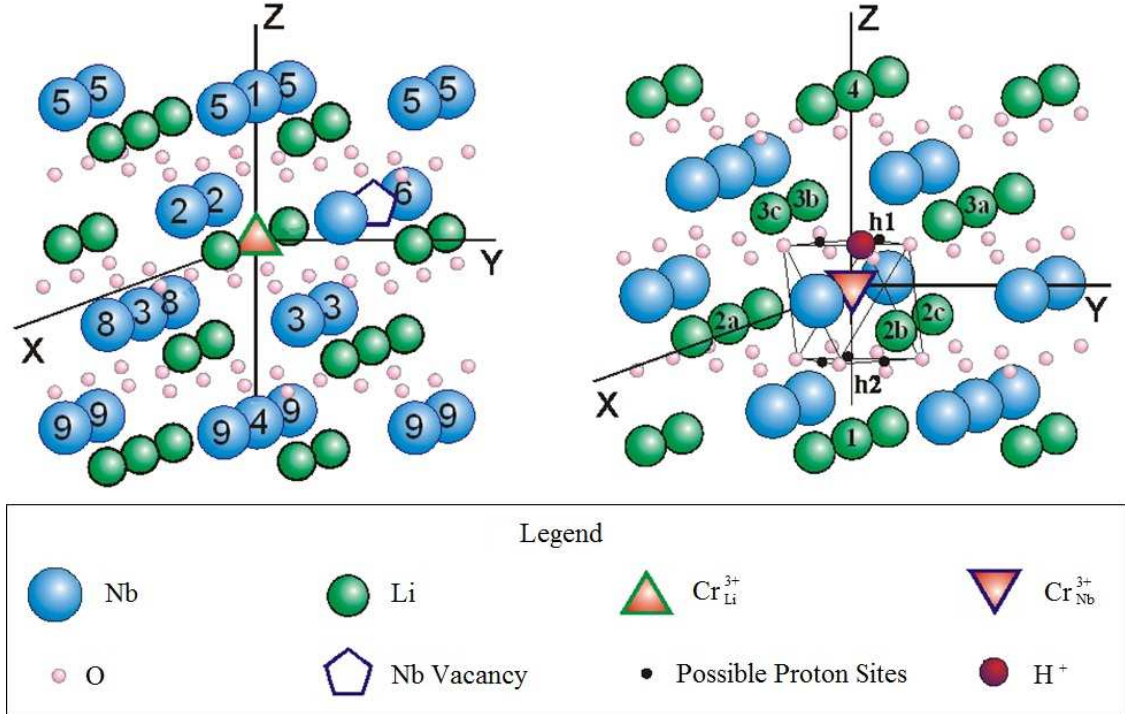
However, the presence of such a high concentration of Mg adds even more disorder to the crystal and this has the effect of broadening the EPR spectra, making it difficult to accurately characterize the observed centers. For greater detail and accuracy, a stoichiometric sample was also studied. An article studying the differences in the useful properties depending on the material composition has been published.¹⁰ The lack of defects in the stoichiometric material results in very narrow EPR lines.¹¹ This meant that even though the stoichiometric sample only had half the Fe, the lines were just as intense, if not more intense, and overlapped much less.

Several centers were shared by both compositions, and so the stoichiometric material can provide better data for studying centers observed in the congruent material. However, the stoichiometric sample contained several additional centers. These centers have also been observed previously in stoichiometric $\text{LiNbO}_3\text{:Fe}$,¹² but not in stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$. These centers are required in the material in order to achieve the desired Fe concentration, as they help account for the main centers' charge

deficit by substituting at different locations. In this way, these additional centers can be viewed as an effect of the low intrinsic defect concentration of stoichiometric material.

For congruent $\text{LiNbO}_3\text{:Cr}$, it was known that the most dominant center was Cr also located on a lithium site, however there were also several low intensity lines observed. These had obvious non-axial symmetry. Previous research indicated that these centers actually disappear in the stoichiometric composition and so they were initially interpreted as single Cr ions with a non-stoichiometric defect in the nearest neighborhood.¹³ Figure 3 below illustrates a center model presented in a previous publication, where $\text{Cr}_{\text{Nb}}^{3+}$ was observed.¹⁴

However, a study of congruent $\text{LiNbO}_3\text{:Cr}$ with a wide variety of Cr concentrations showed that these centers only appear for higher concentrations of Cr. This seemed to suggest that these small intensity lines are actually Cr pairs.¹⁵ The most likely explanation for these EPR lines then became that they belonged to $\text{Cr}_{\text{Li}}^{3+} - \text{Cr}_{\text{Nb}}^{3+}$, since this is a self compensating pair. Indeed, this center was studied through optical methods¹⁶ and may be the most common configuration for the Cr pairs in these samples, but this center cannot explain the non-axial nature of the centers observed through EPR. It is clear that the new model presented in this thesis must be used to explain all the features of the Cr pairs observed in the EPR spectra.

Figure 3 – Previous Analysis of Non-Axial EPR Lines in LiNbO₃:Cr

The model on the left shows a Cr_{Li} with a Nb vacancy in the near surroundings, while the figure on the right shows a model with Cr_{Nb} with an H⁺ in the nearest surroundings.

Basics of Electron Paramagnetic Resonance

For this section of the introduction, a basic introduction to the theory of EPR is presented. First, there is a model for an EPR experiment using concepts from classical electricity and magnetism, then there is the quantum mechanical explanation, and last there is a brief description of the experimental equipment used.

EPR – Classical Description

For the most basic picture of EPR, we begin with a single free electron experiencing a uniform external magnetic field $\vec{B}_0$. The electron will have a magnetic

moment $\vec{\mu}_s$ and this magnetic moment will experience a torque due to $\vec{B}_0$. This causes the spinning electron to precess about the direction of $\vec{B}_0$. The rate of precession is the well known Larmour frequency $\omega_{Larmor} = \frac{ge}{2m_e} B$, where g is the spectroscopic Lande g -factor, e is the charge of an electron, m_e is the mass of an electron, and B is the magnitude of $\vec{B}_0$. For the free electron, $g = 2.0023$, however for ions in materials the effective value can deviate largely from the free electron value, and in the most general situation g is a tensor.

The electron's dipole moment is equal to $\vec{\mu}_s = -g\mu_B\vec{S}$, where $\mu_B = \frac{|e|\hbar}{2m_e}$

(or $\mu_B = \frac{|e|\hbar}{2m_e c}$ in Gaussian units) is the Bohr magneton and $\vec{S}$ is the spin of the electron.

Classically, the energy of the dipole in $\vec{B}_0$ will be equal to $H_0 = -\vec{\mu}_s \cdot \vec{B}_0 = \vec{B}_0 \cdot \vec{\mu}_s$, which is equal to $H_0 = -g\mu_B\vec{B}_0 \cdot \vec{S}$. This suggests a continuum of possible energy values, but from quantum mechanics the component m_s of $\vec{S}$ in the direction of $\vec{B}_0$ can actually only take two values, $m_s = \pm \frac{1}{2}$, leading to the convention that electrons are spin one-half particles, $S = \frac{1}{2}$. For ions which can have higher magnitudes of spin, m_s can take $2S+1$ different values.

Since the charge of an electron is negative, when $m_s = +\frac{1}{2}$ the component of the dipole $\vec{\mu}_s$ in the direction of $\vec{B}_0$ points opposite $\vec{B}_0$, requiring more energy. Assuming

that the electron is initially precessing in the less energetic mode, we can drive the electron into precessing in the higher energy mode using a second magnetic field $\vec{B}_1$ which oscillates with frequency ν in the plane perpendicular to $\vec{B}_0$. $\vec{B}_1$ will successfully drive the electron into the more energetic mode of precession when ν equals the Larmour frequency. This is known as the resonance condition, and the energy absorbed by the electron will be equal to:

$$h\nu = g\mu_B B_0. \quad (2)$$

This was for a free electron; however when we deal with real ions inside materials, there can be additional fields which add to or subtract from the field B_0 which we apply externally. This means that the EPR resonance condition for the ions' electrons will be met for different values of B_0 , giving rise to a shift in the effective value of g . From this information we can learn about what fields the electrons are experiencing from their surroundings. In fact, this shift will depend on how the material is oriented with respect to B_0 , and so the most general treatment uses g as a tensor.

EPR – Quantum Mechanical Description

From quantum mechanics, it is accepted that electrons possess an intrinsic spin $S = \frac{1}{2}$. Also from quantum mechanics it is accepted that only one component of the spin vector can be known due to the non-commutative relationships of the relevant operators. The component which is effectively measured in an EPR experiment will be the component of $\vec{S}$ in the direction of $\vec{B}_0$, customarily taken to be the z-direction. This

component is denoted m_s . This component m_s can only have values $\pm \frac{1}{2}$ in units of $\hbar$.

Accordingly, the energy $H_0 = \vec{B}_0 \bullet \vec{\mu}_s$ can only have discrete values.

In the classical picture the term precessional mode was used, here we must speak of spin eigenstates of H_0 . Then, the field $\vec{B}_1$ will give rise to a perturbation potential H_{pert} . If $B_1 = \cos(2\pi\nu t)$, then $H_{pert} = g\mu_e S_x \cos(2\pi\nu t)$. Here, the operator $S_x = S_+ + S_-$ is defined using creation/annihilation operators $S_+ = \frac{1}{2}(S_x + iS_y)$ and $S_- = \frac{1}{2}(S_x - iS_y)$. This perturbation potential H_{pert} provides the required energy for transitions between the two spin eigenstates of H_0 . The probability of transitions between spin states is proportional to

$$\left| \langle s+1 | H_{pert} | s \rangle \right|^2 = \frac{1}{4} \hbar^2 g^2 \mu_e^2 \cos^2(2\pi\nu t) [S(S+1) - s(s+1)] \quad (3)$$

and

$$\left| \langle s-1 | H_{pert} | s \rangle \right|^2 = \frac{1}{4} \hbar^2 g^2 \mu_e^2 \cos^2(2\pi\nu t) [S(S+1) - s(s-1)]. \quad (4)$$

In most EPR experiments, the frequency ν is held constant, and then the magnitude of $\vec{B}_0$ is varied. When $\vec{B}_0$ is at the required value according to the resonance condition, eq. (2), the transition from lower energy eigenstate to higher energy eigenstate can occur and this can be detected as an increase in the rate of microwave energy absorbed inside the spectrometer resonant cavity.

This most basic picture of EPR was for a single electron, subject only to magnetic fields $\vec{B}_0$ and $\vec{B}_1$, however for actual ions in free space there is also the possibility of fine

structure or spin-orbit interaction which splits the degenerate energy states even before the application of $\vec{B}_0$. There could also be hyperfine interaction between the electron cloud and the ionic nucleus $\vec{S} \bullet A \bullet \vec{I}$, where $\vec{I}$ is the nuclear spin vector and A is the hyperfine interaction tensor. The magnetic isotopes for both Fe and Cr are of relatively small concentrations and for these ions the hyperfine interaction A is too small to be resolvable.

Even for free, neutral atoms, the spin-orbit coupling means that different orbitals which were previously thought to have the same values of energy are actually non-degenerate. The brief derivation given here very closely follows that given by Gasiorowicz.¹⁷ When an electron moves with velocity $\vec{v}$ through the electric field $\vec{E}$ produced by its nucleus, it experiences an additional magnetic field given by

$$\vec{B}_{s.o.} = \frac{-\vec{v} \times \vec{E}}{c^2} = -\frac{1}{c^2} \vec{v} \times \frac{\vec{r}}{r} \frac{d\phi(r)}{dr}, \quad (5)$$

where $\phi(r)$ is the electric potential due to the nucleus. We want this potential only in terms of $\vec{S}$ and $\vec{L}$. Using $\vec{\mu}_s = -\frac{e\hbar}{2m} g \vec{S}$ with $g \simeq 2$ so that $\vec{\mu}_s = -\frac{e\hbar}{m} \vec{S}$, and also the definitions of linear momentum $\vec{p}$, and angular momentum $\vec{L}$:

$$\vec{\mu}_s \bullet \vec{B}_{s.o.} = \frac{e\hbar}{m} \vec{S} \bullet \vec{v} \times \vec{r} \frac{1}{c^2 r} \frac{d\phi(r)}{dr} = \frac{e\hbar}{m^2 c^2} \vec{S} \bullet \vec{p} \times \vec{r} \frac{1}{r} \frac{d\phi(r)}{dr} \quad (6)$$

$$= -\frac{e\hbar}{m^2 c^2} \vec{S} \bullet \vec{L} \frac{1}{r} \frac{d\phi(r)}{dr}. \quad (7)$$

Using the potential due to the nucleus $\phi(r) = \frac{Ze}{4\pi\epsilon_0 r}$,

$$-\vec{\mu}_s \cdot \vec{B} = \frac{1}{m^2 c^2} \frac{Ze^2 \hbar}{4\pi\epsilon_0} \frac{\vec{S} \cdot \vec{L}}{r^3}. \quad (8)$$

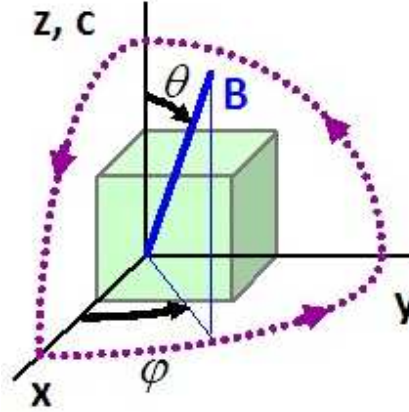
This is not quite finally correct; the relativistic Thomas precession factor must be included, which multiplies the above by $\frac{1}{2}$.

Finally, there is the interaction between the ion and the material crystal field. For both Cr and Fe in LiNbO_3 , this will actually have a greater effect than any other (before the application of $\vec{B}_0$) on the correct energy levels for the ground states of the ions. This will lead to EPR spectra having a strong dependence on the sample's orientation with respect to the external $\vec{B}_0$ field.

Rotating the sample with respect to the direction of the external magnetic field is the only option for completely characterizing the effects of the crystal field. This is usually done by scanning EPR spectra with one or two degree steps in all three planes so that the complete angular dependence of the EPR spectra can be observed. The final collection of spectra combined from all three planes is often referred to as a road map. Figure 4 below illustrates the three rotations, where θ and φ are polar and azimuthal angles.

Next, it is necessary to deal with the ions' electronic configurations, which determine what spin the ions have. Neutral chromium is an exception to the Aufbau Principle and has the ground state configuration $[\text{Ar}]3d^5 4s^1$. Then Cr^{3+} has the electron

Figure 4 – Road Map Rotations



The figure above illustrates the three ninety degree rotations, one about each axis, which must be studied in order to completely characterize the effects of the crystal field.

configuration $[\text{Ar}]3d^24s^1$ which has $S = \frac{3}{2}$. Fe^{3+} has the configuration $[\text{Ar}]3d^54s^2$, which

has $S = \frac{5}{2}$. These are high spin ions, and they can be affected by many different fields

within a sample. Interactions between the high spin ions with other nuclei and magnetic fields are described using the relativistic spin-Hamiltonian of quantum mechanics:

$$H = \mu_B \vec{B} \sum_i g^{(i)} S^{(i)} + \sum_{i,pq} B_p^q O_p^q(S^{(i)}) + \sum_{i>k} S^{(i)} J^{(ik)} S^{(k)} - \vec{B} \sum_j \mu_n^{(j)} g_n^{(j)} I^{(j)} + \sum_{j,pq} Q_p^q O_p^q(I^{(j)}) + \sum_{i,j} S^{(i)} A^{(ij)} I^{(j)} \quad (9)$$

Here, $\vec{I}$ is the nuclear spin vector, μ_n is the nuclear magneton, i and k are the electron spin numbers, j is the nuclear number, B_p^q are parameters for the internal crystal field with $p = 2, 4, 6$ and $-p \leq q \leq p$, $O_p^q(S)$ and $O_p^q(I)$ are irreducible tensor operators, Q_p^q are parameters for quadrupole interaction, and finally J and A are the tensors for exchange and hyperfine interactions.

The first term accounts for Zeeman interactions, the second accounts for the effects of the crystal field, the third is important for analyzing the spectra from the Cr pairs since it accounts for exchange interactions between two spin-magnetic ions, the fourth accounts for nuclear Zeeman interactions, the fifth accounts for nuclear quadrupole interactions, and the last accounts for hyperfine interactions. If these spin matrices have a rank higher than $2S$, and then they vanish. The specific spin-Hamiltonians used for Cr and Fe are thus comparatively simplified, and will be discussed later. As it is, the number of parameters required to accurately fit the observed angular dependences can be huge. For further information on the spin-Hamiltonian, see references 18, 19, and 20.

EPR – Experimental Equipment

There are many different makes and models of EPR spectrometers, but the majority of them share many of the same basic elements. To begin, there is a microwave energy source which provides the oscillating B_1 field, and this is connected via a waveguide to a resonant cavity. This cavity is where the sample is mounted, and the cavity creates a standing wave out of the microwave energy, rather than a travelling wave. There are various modes and sizes of cavities in wide use, and the frequency of microwaves from the source must match the resonant frequency of the cavity. The process of matching the frequency is called tuning, and the goal is to achieve the highest possible quality factor. Then, this frequency is held constant during the EPR experiments.

Next, the cavity should be in between two large electromagnets which are powered by a current source. The current source allows for the strength of the external

B_0 field to be scanned over the desired ranges for the experiment. The current can be very high ($\simeq 50 - 100$ amperes), meaning that the electromagnets are commonly water cooled. Finally, there should be some method of recording the spectra as the external field strength is swept.

The spectrometer used to study both $\text{LiNbO}_3\text{:Mg:Fe}$ samples was a Varian E-109, and the $\vec{B}_1$ field was introduced using a standing wave in a transverse electric mode (TE_{102}) produced within a rectangular cavity. The frequency ν emitted from the microwave bridge was in the X-band range (9.4 GHz), produced by a klystron source. In the TE_{102} mode, the electric field of the microwave energy oscillates horizontally with a node at the sample location, while the magnetic field oscillates vertically with two nodes and at the sample location there is an anti-node oscillating vertically, perpendicular to $\vec{B}_0$. The $\vec{B}_0$ field was provided by current coils creating a uniform horizontal field at the sample location.

The Varian E-109 is an old spectrometer, originally built well before the information age. It is now equipped with a Platform Independent Data Acquisition Module (PIDAM) from Scientific Instruments. This allows for the spectra to be recorded digitally and analyzed using software developed by Prof. Valentyn Grachev for use by members of Prof. Galina Malovichko's group. Figure 5 below shows the Varian spectrometer.

For the $\text{LiNbO}_3\text{:Cr}$ sample, an ultra-modern Bruker Elexsys E560 spectrometer was used. This spectrometer has the ability to produce double the $\vec{B}_0$ field strength, which

allows the use of higher $\vec{B}_1$ frequencies. Two microwave bridges and cavities were used, one was a cylindrical X-band (9.5 GHz) supercavity and the other was a cylindrical Q-band (34.4 GHz) cavity. Both microwave bridges utilize microwave diodes as sources.

Figure 5 – Varian E-109 EPR Spectrometer

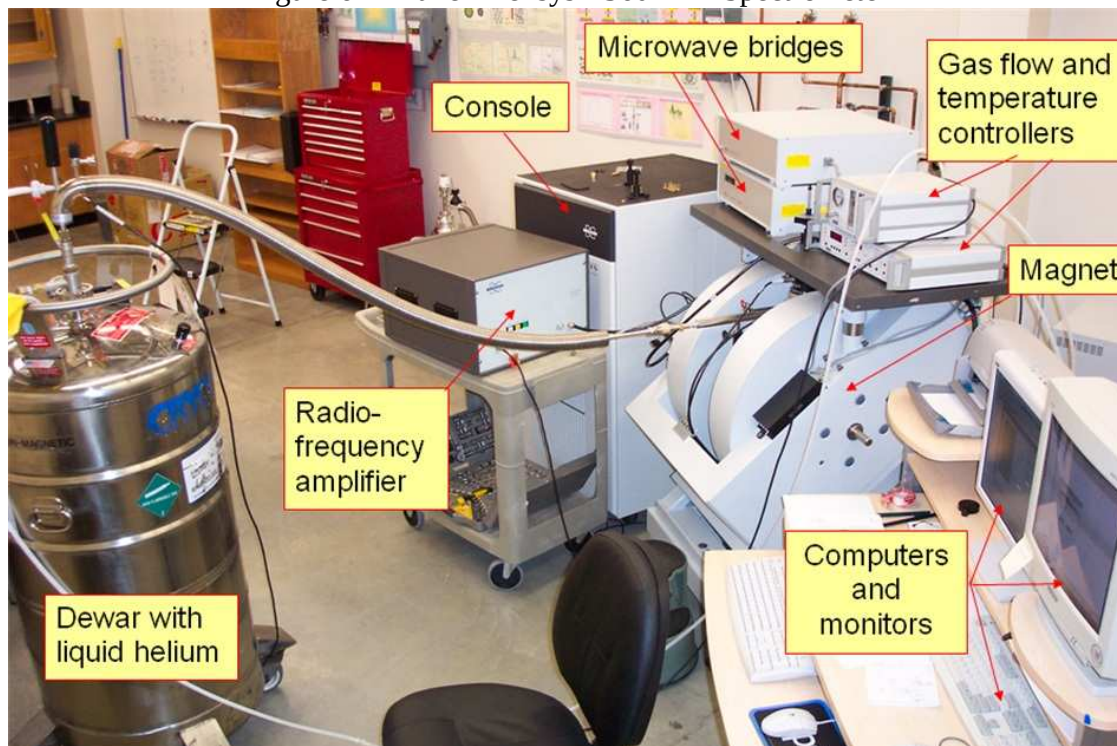


The upper picture shows from left to right the control console with the PIDAM on top of it, then the microwave bridge with the brass waveguide going down in between the electromagnets, and finally the current supply for the electromagnets. The lower picture shows the computer monitor next to the control console and the PIDAM.

Both cavities have liquid helium cryostats, which enable them to conduct experiments at very low temperatures, ranging from 4.2 K up to room temperature. Finally, the spectrometer has two cavities capable of ENDOR experiments, but these were not utilized for this thesis. This spectrometer was of course designed with computers in mind and the spectrometer is operated using software created by Bruker.

The data is then converted to a more useful format and analyzed using the same software package as for the Varian spectrometer. Figure 6 shows the Bruker spectrometer.

Figure 6 – Bruker Eleksys E560 EPR Spectrometer



The figure above shows the Bruker spectrometer prepared for low-temperature experiments. Both microwave bridges can be seen above the electromagnets, as well as the liquid helium dewar and transfer line. The radio-frequency amplifier is used for ENDOR experiments, and not utilized for this thesis.

DATA & ANALYSIS

For this thesis, hundreds of spectra had to be recorded. For each sample it was necessary to scan the entire angular dependence using one or two degree steps. Rotating through 90 degrees in all three planes gives a total of 135-270 spectra per sample. The congruent $\text{LiNbO}_3\text{:Mg:Fe}$ sample was studied using two degree steps (135 spectra), while the stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$ sample was studied using one degree steps (270 spectra). The congruent $\text{LiNbO}_3\text{:Cr}$ was also studied using one degree steps for both X-band (9.5 GHz) and Q-band (34.4 GHz) (540 spectra).

This totaled almost one thousand data files. All these spectra were then treated using the “Visual EPR” software package, a collection of several programs used exclusively by members of Prof. Galina Malovichko’s research group, developed by Prof. Valentin Grachev. To begin, start with a single spectrum and find the centers of all EPR spectroscopic lines by setting proper analysis parameters in the software. The program “VIEWSpec” does this, creating a data file with line center positions for that first spectrum. This is called peak picking, and it analyzes and records the line centers, widths and intensities.

Luckily, once proper parameters have been set for one spectrum, all the rest can be analyzed automatically using the same parameters. Once this is done, then all the information about line centers from every spectrum (from a single sample) is combined into a data file known as a road map. This road map shows the angular dependence of the EPR spectra.

The next step is to fit the experimental angular dependence with a calculated one.

This is how the values of g-tensor and crystal field elements are determined. To better explain this, the steps taken to analyze the data from LiNbO₃:Cr are shown in detail. Then the special steps taken to deal with the Cr interaction pairs are shown. Then, the results from LiNbO₃:Mg:Fe are presented, since Fe³⁺ is a high spin ion, and the presence of so many lines in the stoichiometric material makes it difficult to take in at once.

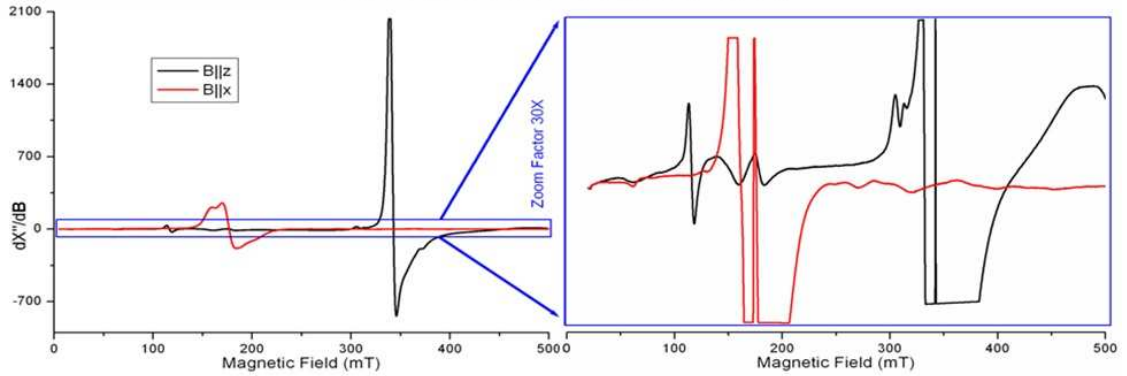
Results from Congruent Lithium Niobate Doped with Chromium

In the LiNbO₃:Cr sample, the main features observed with EPR were attributed to the previously researched main line of Cr³⁺, which has $S = \frac{3}{2}$. Figure 7 below shows representative spectra from both the X-band and Q-band frequencies, for two sample orientations each. The most intense line in all spectra is due to the main Cr center, however once the spectra are recorded with greatly increased gain (“zoom” factor), the small intensity lines can be seen. These lines were the main focus for this thesis. The left side of Figure 7 shows the entire spectrum, while the right side was recorded using much higher gain illustrating the small intensity lines of greatest interest.

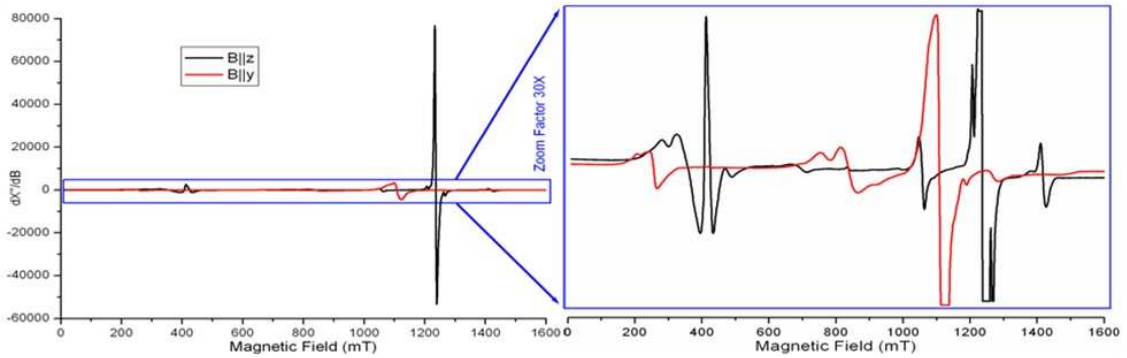
The sample was initially mounted in the microwave resonator so that its crystallographic z-axis was parallel to B_0 . This resulted in the black spectrum in Figure 7 above. Then the sample was rotated about the vertical axis by one degree, and another spectrum was recorded. This was repeated for another 89 spectra until the crystal’s y-axis was parallel to B_0 . This last spectrum is the red spectrum above.

To better illustrate this process, Figure 8 on page 24 shows all the spectra recorded for LiNbO₃:Cr using the Q-band (34.4 GHz) frequency in one plane. Each blue

Figure 7 – Representative Spectra From Congruent LiNbO₃:Cr
EPR Spectra (X-Band, 9.5 GHz)



EPR Spectra (Q-Band, 32 GHz)



Each plot in the figure above displays a spectrum with $B_0||z$ in black and a spectrum with $B_0||y$ in red. Upper left: low gain X-band, upper right: high gain X-band, lower left: low gain Q-band, lower right: high gain Q-band.

line is a single EPR spectrum like the ones shown above in Figure 7, and each line is a spectrum recorded at a different degree. Comparing Figure 7 and 8, it may be possible to discern that the bottom spectrum of Figure 8 is similar to the red spectrum ($B_0||y$) in the lower right side of Figure 7, and the top spectrum of Figure 8 is similar to the black spectrum ($B_0||z$) of Figure 7. Figure 8 is actually the angular dependence in the zx -plane, however, due to the symmetry of the LiNbO₃ lattice, spectra taken with $B||y$ will look almost identical to those with $B||x$, as will become more apparent in the figures to come.

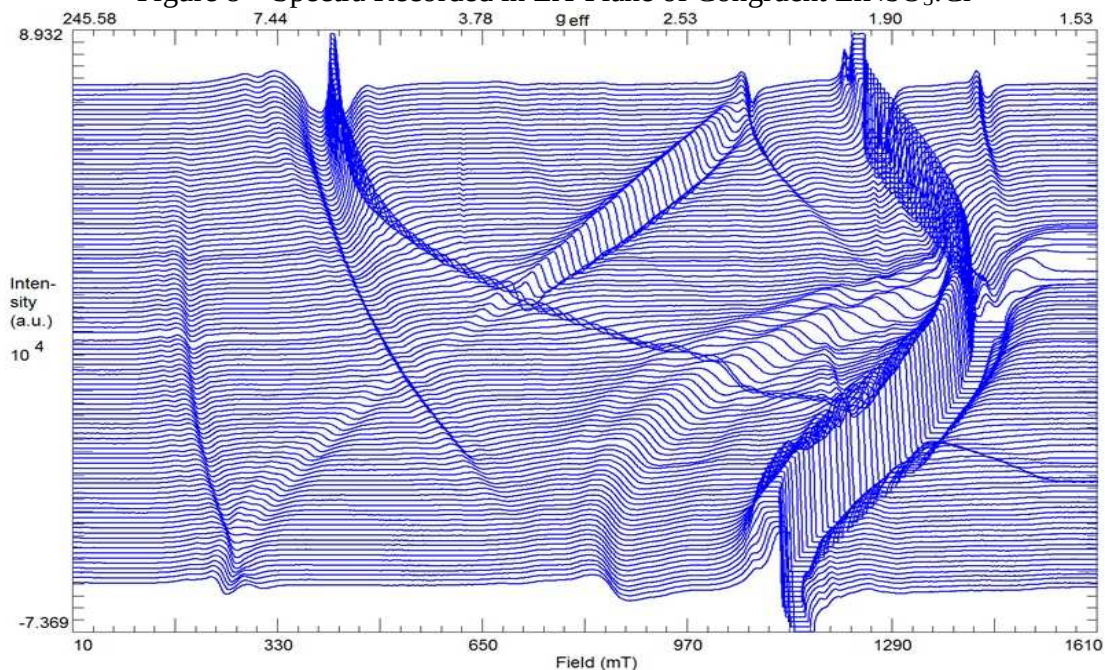
There are actually over 100 degrees recorded and displayed in Figure 8 to ensure

that both axes were included in the angular dependence. When every spectra is displayed side by side in this way, it is possible to see how the spectra change as the sample is rotated. This collection of spectra is called a road map, but a complete road map should include the angular dependences from all three planes.

In this sort of EPR spectroscopy, we are interested in exactly what magnitude of B_0 was necessary to satisfy the resonance condition for spin state transitions. While Figure 8 is good for explaining what an angular dependence means, it is not very good for determining the values of all the parameters of eq. (9). For this, the program “VIEWSpec” is crucial. Figure 9 shows the same spectra after they have been treated using the “ViewSpec” software.

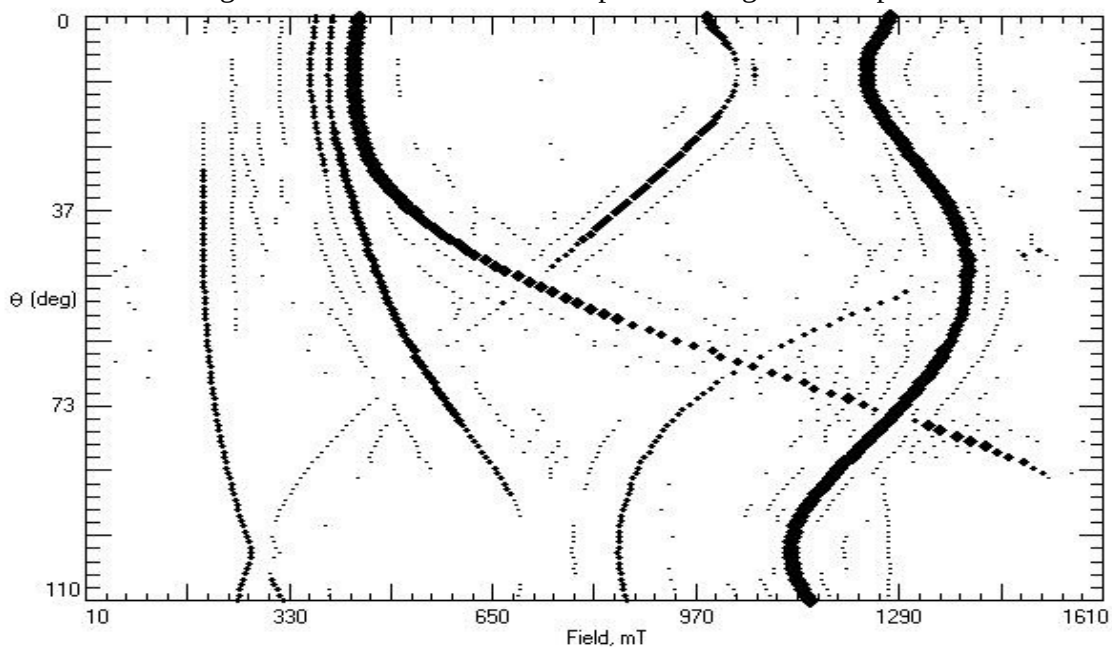
“VIEWSpec” creates a picture like Figure 9 by marking the center of each EPR resonance line with a black symbol, and repeats this for all spectra of a given plane. It is most important to note how the black symbols in Figure 9 below create lines which are identical to the most intense features of Figure 8. These features belong to the most prevalent center in LiNbO₃:Cr, the main $\text{Cr}_{\text{Li}}^{3+}$, which was studied previously.

Figure 10 on page 25 shows the same plot as Figure 9, but highlights how the axes (red lines) of the crystal can be identified, using the fact that the resonance lines are usually at a local maximum or minimum magnitude of B_0 when the crystal axes are parallel with the external $\vec{B}_0$. The small diagram to the right side in Figure 10 illustrates that these spectra were recorded by mounting the sample in the microwave resonant cavity so that the crystal y-axis was vertical, and then rotating about this axis in the z-x plane.

Figure 8 – Spectra Recorded in ZX-Plane of Congruent $\text{LiNbO}_3\text{:Cr}$ 

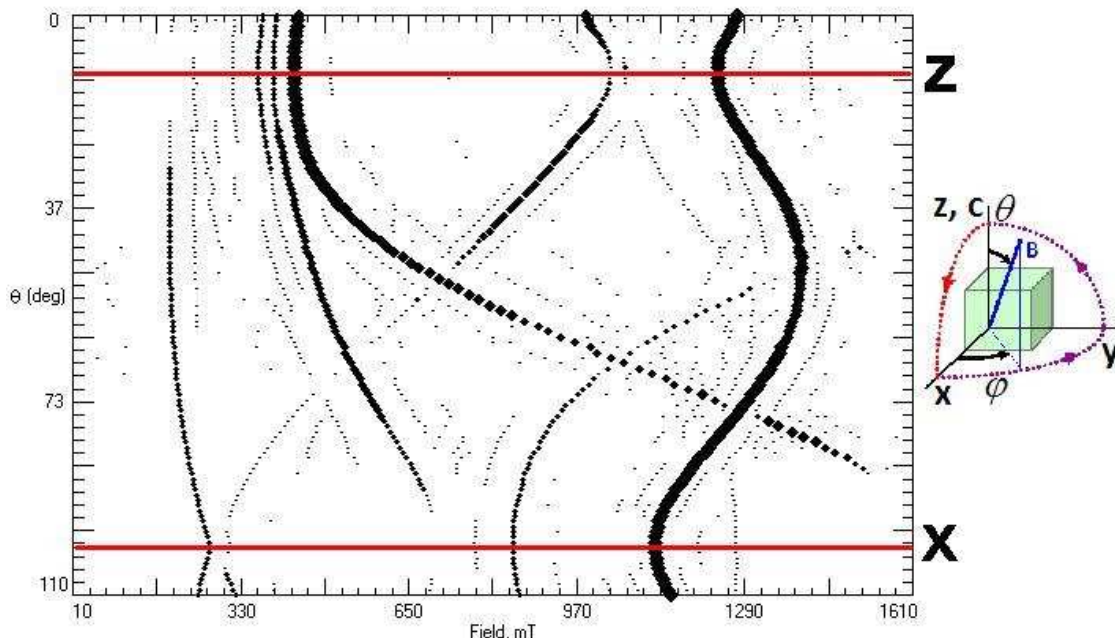
The figure above displays all spectra from the zy-plane of $\text{LiNbO}_3\text{:Cr}$. Note: top and bottom spectra here are similar to the black and red spectra in Figure 7, lower right.

Figure 9 – Initial Treatment of Spectra Using “VIEWSpec”



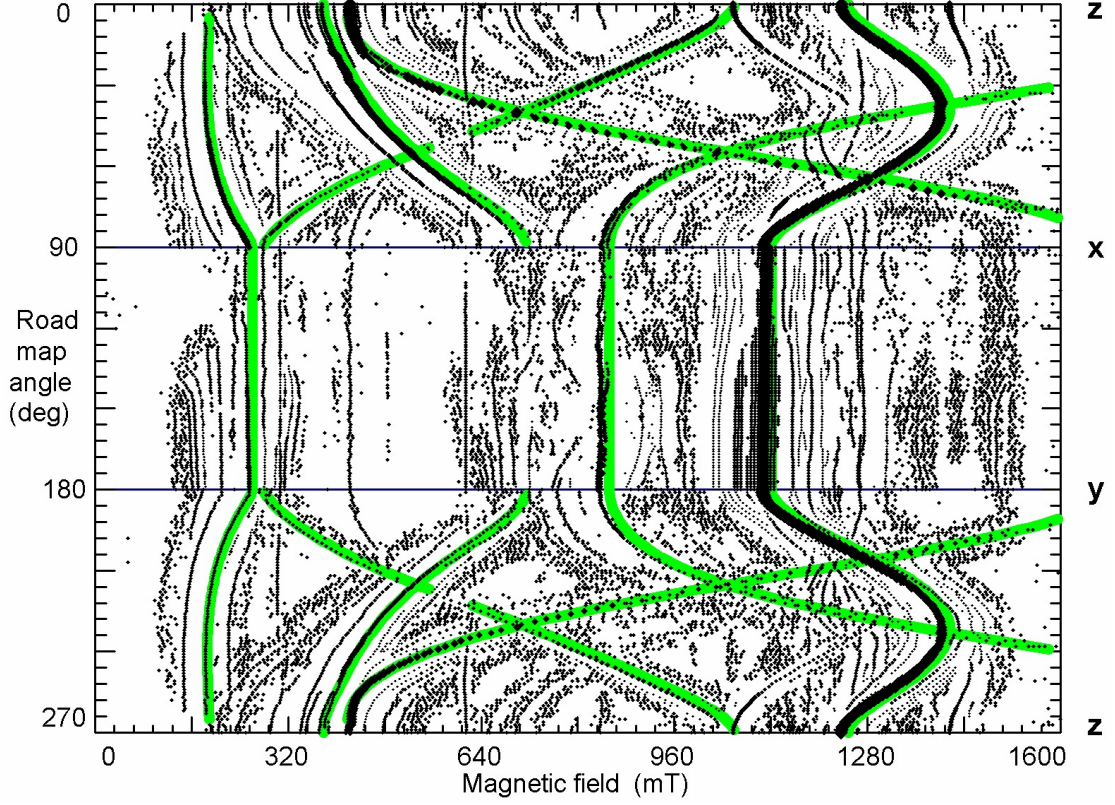
The figure above displays the same spectra as Figure 8 after they have been treated using the “VIEWSpec” program. Note: the symbols here form lines which are identical to the main features of Figure 8.

Figure 10 – Determining the Axes in a Single Plane



The figure above illustrates picking out the axes in the z-x plane by finding local maxima and minima, which correlate to having an axis is parallel to B_0 .

Figure 11 below shows this final road map for Q-band. This figure was made using parameters in “VIEWSpec” which mark the centers of as many spectroscopic lines as possible, as are all future road maps presented in this thesis. Note that the zx- and zy-planes look very similar; this is due to the symmetry of the LiNbO_3 lattice. Also, many lines do not exhibit an angular dependence in the xy-plane. These lines belong to axial centers. The figure also shows green lines which were created using a computational calculation for the angular dependence, after the spin-Hamiltonian parameters were properly fitted.

Figure 11 – Q-band Road Map for LiNbO₃:Cr

The figure above shows the final road map of LiNbO₃:Cr using the Q-band frequency. The green lines were produced using a computer simulation for the angular dependence, after the terms of eq. (9) had been properly fitted.

To create the calculation shown in green on Figure 11 above, the following spin-Hamiltonian was used:

$$H_0 = \mu_B \vec{B}_0 \cdot g \cdot \vec{S} + \frac{b_2^0 O_2^0(\vec{S})}{3}, \quad (10)$$

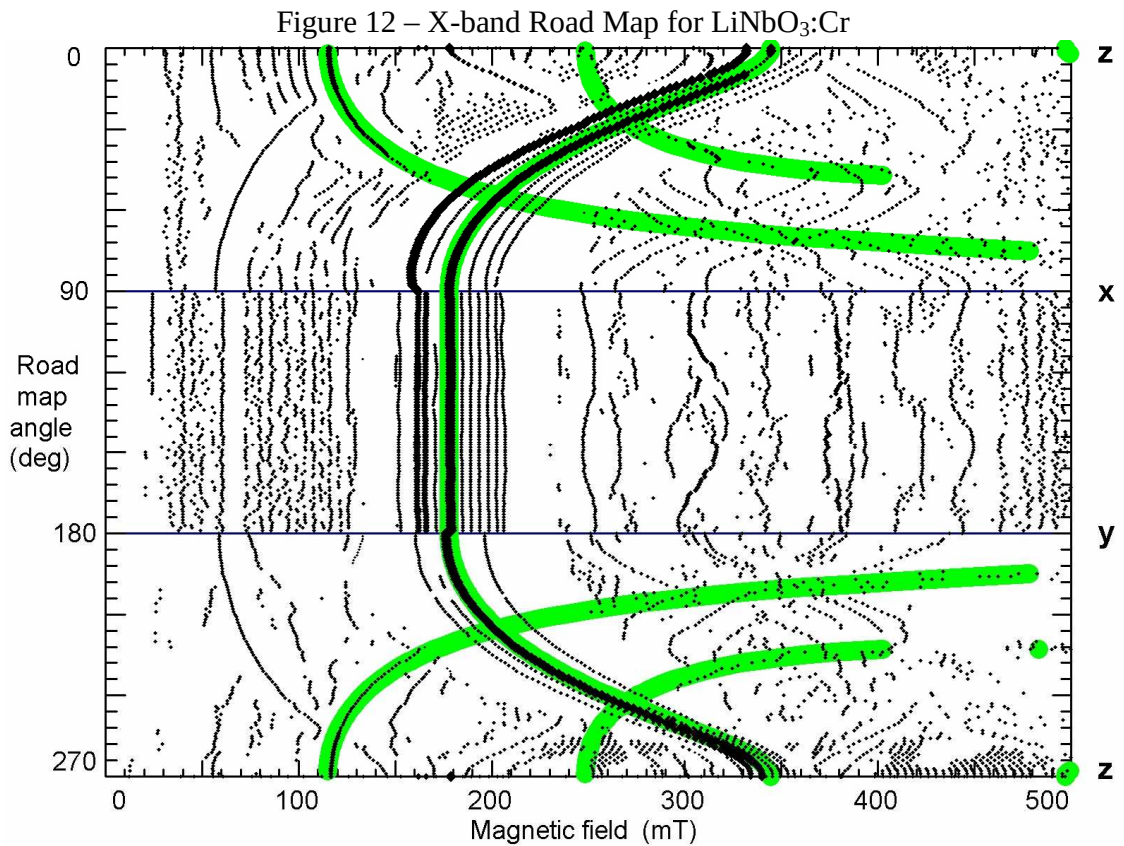
where g = spectroscopic g -tensor, $S = \frac{3}{2}$ for Cr³⁺, b_2^0 = parameters of crystal field and

$O_2^0(\vec{S})$ is the irreducible tensor of electron spin. These are the only non-vanishing terms

of eq. (9) for Cr³⁺ in LiNbO₃. The best fitting was achieved using a zero-field splitting of

0.784 cm^{-1} , $g = 1.995 \pm .005$, $|b_2^0| = 0.391 \pm 0.001$. Again, this is for the main axial Cr^{3+} center, which has been previously studied.

Figure 12 below shows the final road map for X-band (9.5 GHz) after those spectra had received the same treatment as the Q-band spectra had, as well as a computational calculation also in green using the same parameters as in Figure 10, only with the different frequency. It can be seen that these parameters also fit the data for the most intense lines very well, providing good confirmation that the parameters of eq. (10) have been accurately determined.



The figure above is the road map of $\text{LiNbO}_3\text{:Cr}$ using X-band. The green computer simulation lines used the same parameters as in Figure 11 with the new frequency.

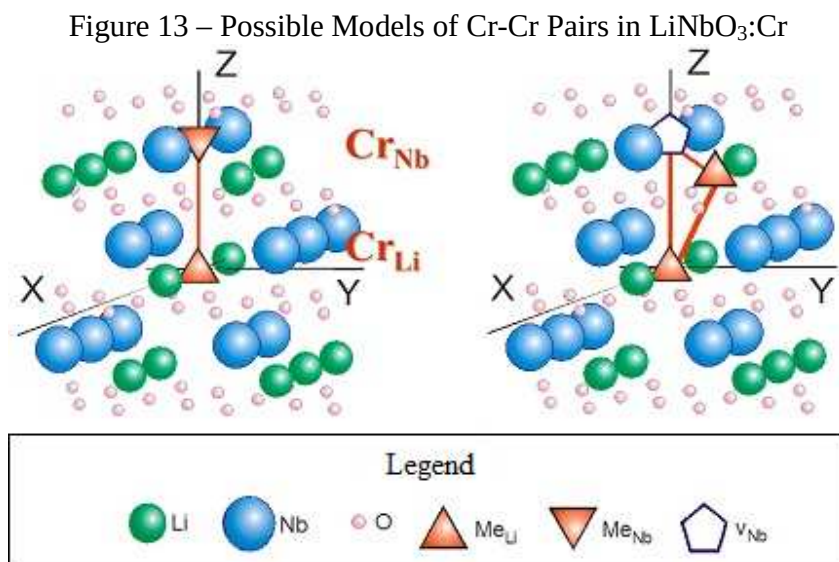
Figures 11 and 12 show good agreement between the experimental data and the calculated angular dependence. However, it is also seen that several features do not belong to the main axial $\text{Cr}_{\text{Li}}^{3+}$ center. Also, the fact that some features show angular dependence when the sample is rotated about the crystallographic z-axis indicates that these features belong to centers with non-axial symmetry. Initial analysis indicates that these centers could be complexes with single Cr ions with a non-stoichiometric defect in the near vicinity, or Cr^{3+} - Cr^{3+} pairs.

One possible model to explain the position of the pairs in the lattice is for them to consist of one Cr^{3+} on a lithium site ($\text{Cr}_{\text{Li}}^{3+}$) and the other on a niobium site ($\text{Cr}_{\text{Nb}}^{3+}$). These are self-compensating nearest neighbor pairs, and so are thought to be the most common pairing of Cr ions. However, this model cannot explain the observed spectra since this model is an axial center.

Another model involves next nearest neighbors with both Cr^{3+} ions on Li sites.²¹ This would leave an excess of charge; the model presented in this thesis uses a Nb vacancy as a nearest neighbor of one of the Cr ions for charge compensation. This overcompensates for the excess charge brought by the $\text{Cr}_{\text{Li}}^{3+}$ - $\text{Cr}_{\text{Li}}^{3+}$ pairs. This final lack of charge can also compensate the main axial $\text{Cr}_{\text{Li}}^{3+}$, allowing even more Cr to enter the crystal, or simply be accounted for by one of the many Li^+ vacancies.

The position of the Nb vacancy is not randomly distributed around the Cr-Cr pair; if it were, it would cause these Cr centers to have much broader lines. Since they have widths narrow enough to be comparable to those for single Cr centers, the Nb vacancy therefore must have a consistent position for every center. The model presented here

suggests that it is along the z-axis above or below one of the Cr-ions. Figure 13 below illustrates the two models for Cr-Cr pairs.

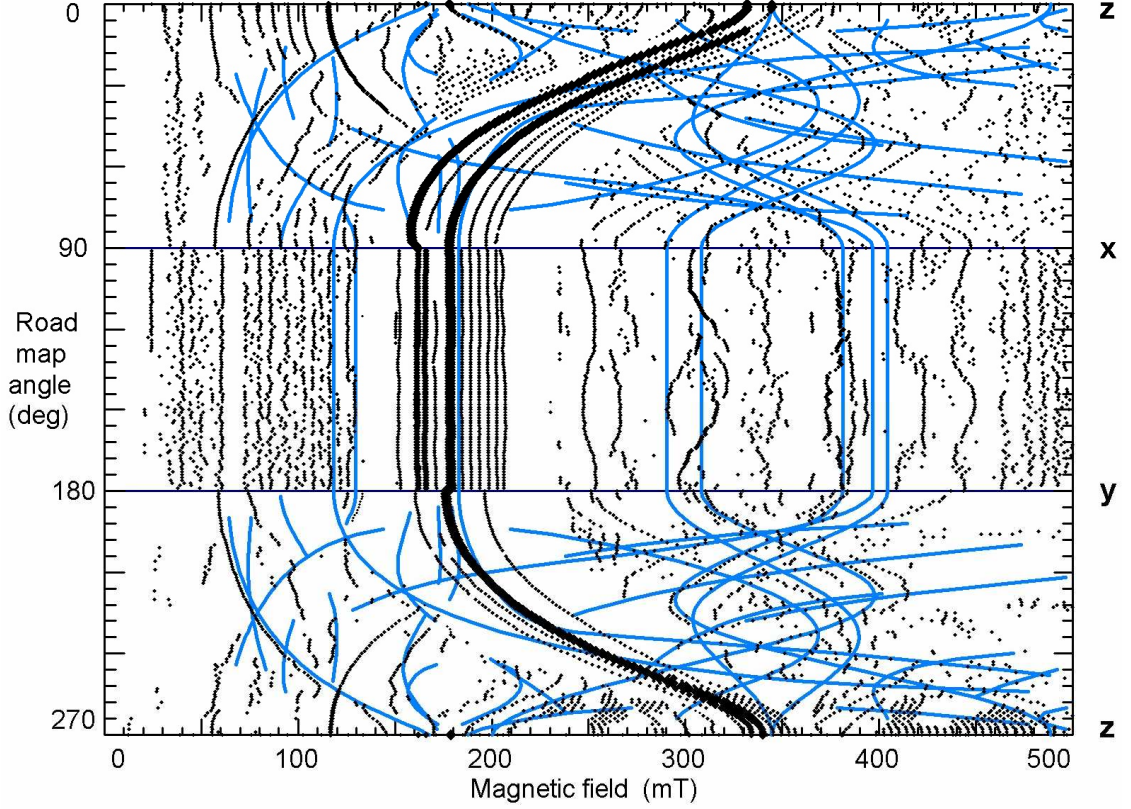


The figure above shows the two models for Cr-Cr pairs in $\text{LiNbO}_3\text{:Cr}$. The left model can be observed using optical techniques, but cannot explain the non-axial nature of the centers observed with EPR. The right model is supported by the data of this thesis.

Figure 14 below shows an early attempt at fitting the pairs observed using the X-band frequency; it can be seen that this calculation shown in blue used an axial symmetry by the lack of angular dependence in the xy-plane. To better fit the actual behavior of the EPR lines, a good understanding of how the spins for the two ions add together is necessary.

Figure 15 on page 31 shows how the spins of hydrogen ions add together. For calculating the angular dependence of two ions with $S_1 = S_2 = \frac{3}{2}$ such as Cr^{3+} , the problem becomes more involved, since there are more possible results for combining two spin

Figure 14 – Initial Calculation to Fit Parameters for Cr-Cr Pairs



The figure above shows an early attempt to fit the data from LiNbO₃:Cr using X-band. The blue lines are a computer simulation using an axial symmetry, which cannot fit the observed behavior of the EPR lines.

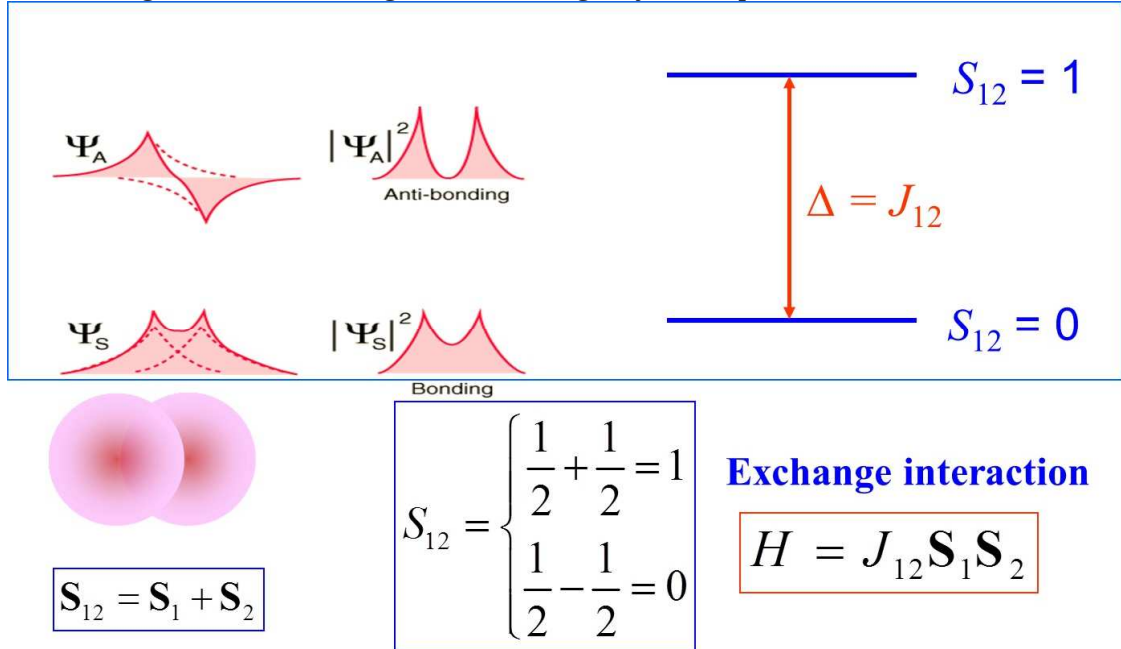
momenta into total spin $S_{12} = S_1 + S_2$. According to the theory of angular momentum

summation, total spin can have the following values:

$$S_{12} \Rightarrow \frac{3}{2} + \frac{3}{2} = 3, \quad \frac{3}{2} + \frac{1}{2} = 2, \quad \frac{3}{2} - \frac{1}{2} = 1, \quad \text{and} \quad \frac{3}{2} - \frac{3}{2} = 0. \quad (11)$$

Therefore, there are four energy levels characterized by their values of total spin S_{12} . In general, distances between these four levels can be described by three independent parameters. In crystals, the characteristics of exchange interactions can be positive or negative and become tensors. Tensor components are determined from the

Figure 15 – Breif Diagram Illustrating Key Concepts for Pair Interaction



The figure above shows several key concepts for pair interaction. The plots of Ψ_A , Ψ_S , $|\Psi_A|^2$, and $|\Psi_S|^2$ show how the hydrogen ground state wavefunctions sum together for bonding and anti-bonding. The energy diagram to the right of those shows that there will be a difference in energy depending on how the wavefunctions add due to the exchange interaction.

sequence, positions and splitting of these energy levels.

The energy levels of two Cr^{3+} ions can be described by the following spin-

Hamiltonian with reasonable accuracy:

$$H_0 = \mu_B \mathbf{B} \cdot (\mathbf{S}_1 + \mathbf{S}_2) + b_{2,A}^0 O_2^0(\mathbf{S}_1)/3 + b_{2,B}^0 O_2^0(\mathbf{S}_2)/3 + \mathbf{S}_1 \cdot J_{12} \cdot \mathbf{S}_2 \quad (12)$$

where J_{12} is the exchange interaction tensor, $b_{2,A}^0$ and $b_{2,B}^0$ are the characteristics of

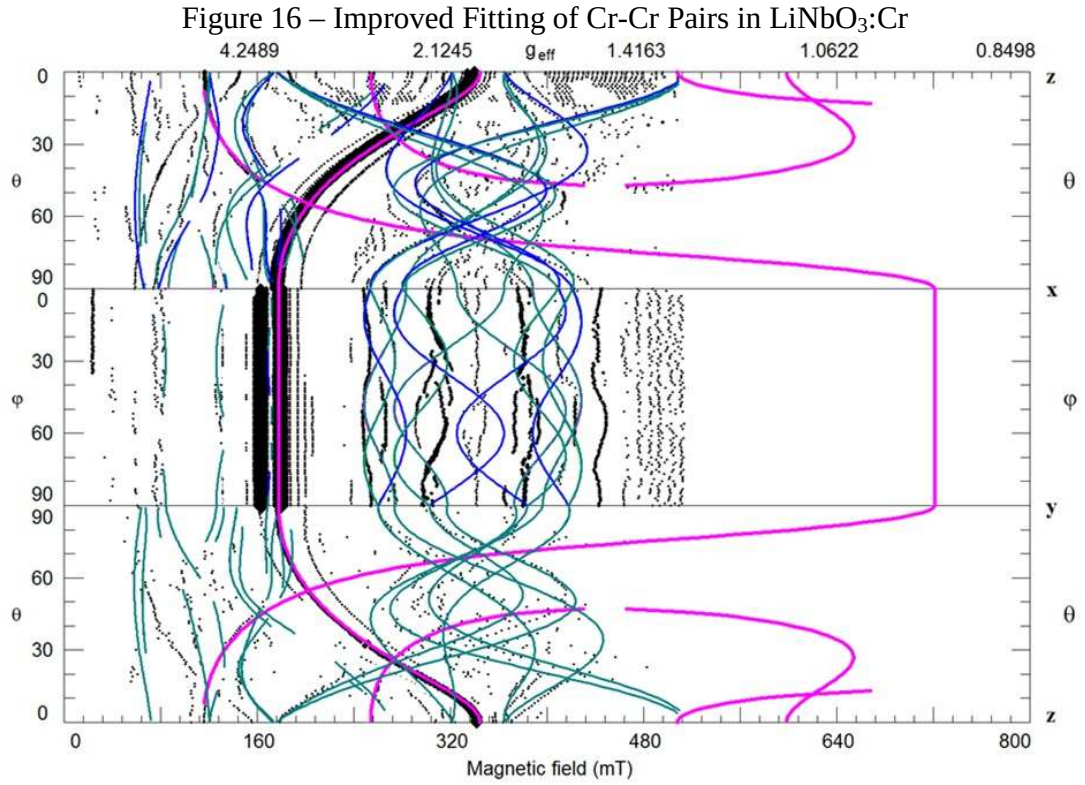
crystal field in the locations of chromium ions (for instance, Li and Nb substitutions). It

is also possible to describe the same energy levels by using the effective spin-

Hamiltonian for every value of total spin:

$$H_0 = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{k=2,4,6; q=0,1,\dots,k} b_k^q(S) O_k^q(\mathbf{S}) / 3 + \sum_{k=2,4,6; q=1,\dots,k} c_k^q(S) \Omega_k^q(\mathbf{S}) / 3. \quad (13)$$

Figure 16 below shows a much improved computational calculation for the Cr-Cr pairs using this spin-Hamiltonian in blue, as well as the main axial Cr center now in magenta including the theoretical behavior of the lines in ranges of $\bar{B}_0$ not actually experimentally recorded.



The figure above shows an improved computational simulation using the spin-Hamiltonian of eq. (13).

According to the theory of exchange pairs, the value of $b_2^0(S)$ must be close to $\frac{b_{2,A}^0 + b_{2,b}^0}{5}$, where $b_{2,A}^0$ and $b_{2,B}^0$ are axial crystal field parameters of the first and second ions in the pair. A pair consisting of $\text{Cr}_{\text{Li}}^{3+}$ with $b_{2,\text{Li}}^0 = 0.387 \text{ cm}^{-1}$ and $\text{Cr}_{\text{Nb}}^{3+}$ with $b_{2,\text{Nb}}^0 =$

0.0215 cm⁻¹, should have $b_2^0(3) = (0.387+0.0215)/5 = 0.082$ cm⁻¹, whereas a pair consisting of two Cr_{Li}³⁺ should have $b_2^0(3) = 2*0.387/5 = 0.155$ cm⁻¹. The last value is very close to the measured value of 0.164 cm⁻¹, therefore we can now say that the observed pairs are complexes of two Cr_{Li}³⁺ – Cr_{Li}³⁺. This confirms the model which uses a Nb vacancy for charge compensation, with the vacancy always on the z-axis in the complex.

The Table 1 below displays the Parameters of the spin-Hamiltonian for chromium pair in the S = 2 state.

Table 1
Spin-Hamiltonian Parameters for Cr-Cr pairs observed using EPR

Parameter	Value
G00	1.97000
G20	0.00001
G22	0.00001
b20	-280.000
b21	1.000
c21	240.000
b22	40.000
c22	1.000
b40	640.000
b41	1.000
c41	-340.000
b42	800.000
c42	1.000
b43	1.000
c43	-500.000
b44	-1200.000
c44	1.000

Results from Lithium Niobate Codoped with Magnesium and Iron

Iron in lithium niobate usually comes in two charge states: Fe^{2+} and Fe^{3+} .

However Fe^{2+} is not observable by EPR for two reasons. First, Fe^{2+} has orbital momentum $L=2$ and thus a non-zero orbital moment. This interacts strongly with the crystal field even without the application of $\vec{B}_0$. The energy of the applied microwave B_1 is much smaller than the zero-field splitting between energy levels with $\Delta m_s = \pm 1$. Second, EPR transitions between the doublet levels which do not split due to the crystal field are forbidden since for these states $\Delta m_s = \pm 2$. Fe^{3+} however has $L=0$, and $S=5/2$. It is therefore concluded that all Fe observed by EPR were Fe^{3+} .

This higher spin brings its own problems, however, since the spin – Hamiltonian will require more non-zero terms. The spin – Hamiltonian will have rank $2S+1 = 6$. Since the zero field splitting and Zeeman splitting are now comparable, the energy levels cannot be calculated by perturbation theory. Again, the special software developed for use by members of Prof. Galina Malovichko's research group is absolutely required to numerically diagonalize the spin-Hamiltonian matrices. For C_3 symmetry, the spin Hamiltonian has the form:

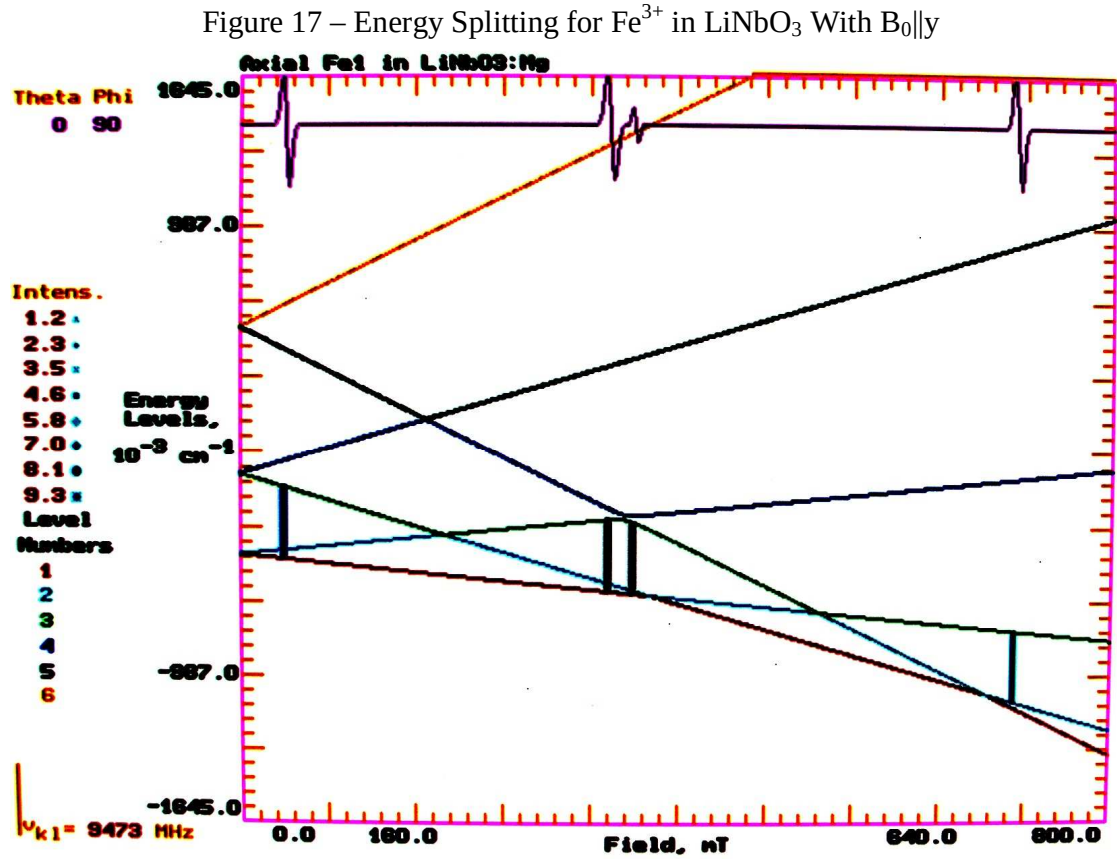
$$H_0 = \mu_B \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{S} + b_2^0 O_2^0(\mathbf{S}) / 3 + b_4^0 O_4^0(\mathbf{S}) / 60 + b_4^3 O_4^3(\mathbf{S}) / 60 + c_4^3 \Omega_4^3(\mathbf{S}) / 60, \quad (14)$$

while for C_1 symmetry, the spin Hamiltonian will include the following terms:

$$\begin{aligned} H_0 = \mu_B \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{q=0,1,2} b_2^q O_2^q(\mathbf{S}) / 3 + \sum_{q=1,2} c_2^q \Omega_2^q(\mathbf{S}) / 3 \\ + \sum_{q=0,1,2,3,4} b_4^q O_4^q(\mathbf{S}) / 60 + \sum_{q=1,2,3,4} c_4^q \Omega_4^q(\mathbf{S}) / 60 \end{aligned} \quad (15)$$

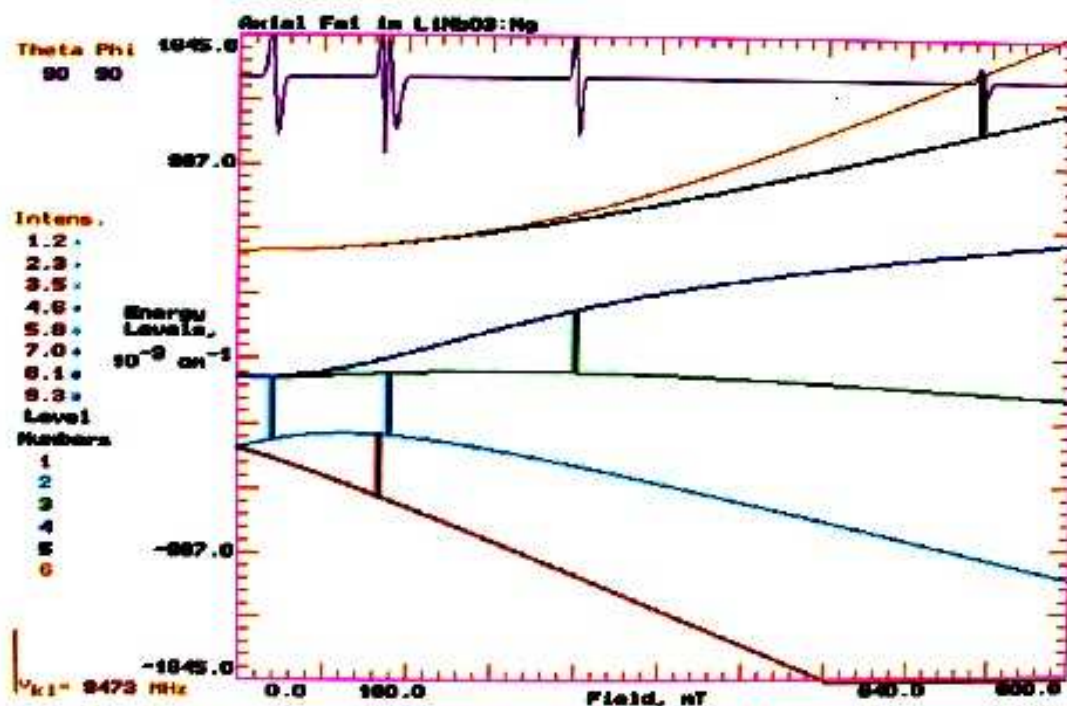
The calculation of energy splitting for when the crystal axes z and y are parallel

to $\vec{B}_0$ are shown below in Figures 17 and 18 (having x parallel to B_0 looks identical to the splitting when y is parallel, and so is not shown).



The above figure shows a computer simulation of the energy splitting as functions of B_0 . This was now necessary due to the large interaction with the crystal field.

The fact that Fe^{3+} has $S = 5/2$ causes some interesting features in the EPR spectra not observable for Cr^{3+} . The $b_4^3 O_4^3(S)/60$ term has the effect of splitting lines in the zx plane, and the $c_4^3 \Omega_4^3(S)/60$ term leads to an asymmetry in the zy plane. The first term technically gives an asymmetry in the zx plane, but this is undone by the glide mirror plane of LiNbO_3 . The observed angular dependence in the zx plane will be a

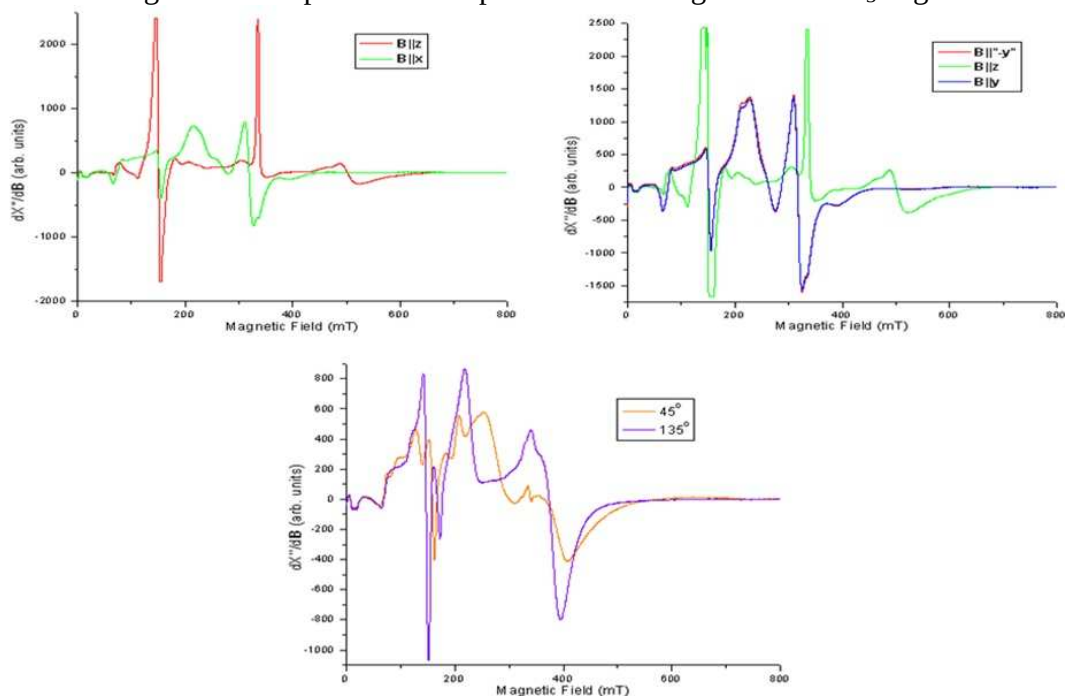
Figure 18 – Energy Splitting for Fe^{3+} in LiNbO_3 with $B_0 \parallel z$ 

The above figure shows a computer simulation of the energy splitting as functions of B_0 . This was now necessary due to the large interaction with the crystal field.

symmetrical sum of asymmetric dependences.

Several representative spectra from the congruent sample are shown below in Figure 19, illustrating the asymmetry described above. Note the very broad and often overlapping lines due to the intrinsic defects and additional disorder introduced by the presence of Mg.

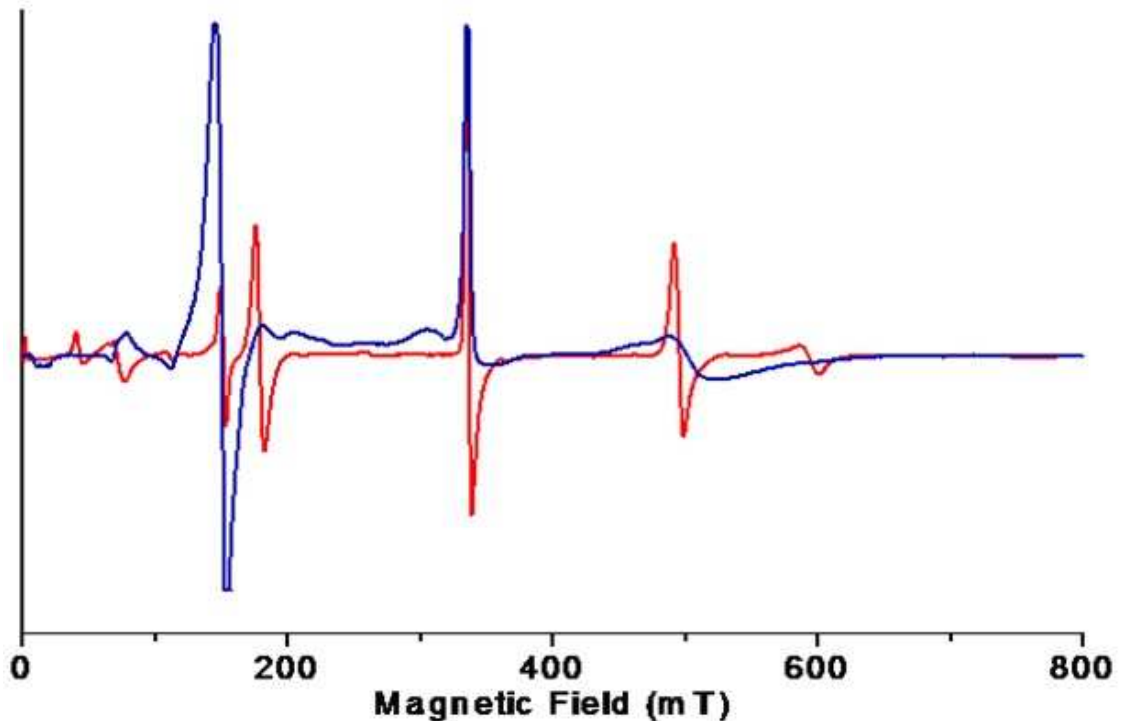
To better characterize the lines observed in the congruent sample, a stoichiometric sample was also studied. Figure 20 on page 38 shows a comparison of spectra from both samples, for the same sample orientation with respect to B_0 . Note that the figure normalizes the intensity of the spectra; the narrower red line from the stoichiometric sample was also more intense.

Figure 19 – Representative Spectra From Congruent $\text{LiNbO}_3\text{:Mg:Fe}$ 

The figure above shows several spectra from the congruent sample of $\text{LiNbO}_3\text{:Mg:Fe}$. In the bottom plot, the two spectra are recorded 90 degrees from each other, equal distances from an axis, and yet are not equivalent. This asymmetry is due to the presence of an oxygen ion, and detectable now by Fe^{3+} due to the high spin value.

To fully appreciate the greater detail offered by the stoichiometric sample, Figure 21 on page 39 shows the same spectrum that appears in red above by itself on the left, and on the right it was recorded with much greater gain. Note that the lines are much more narrow, but that there are also several small intensity lines. These belong to additional centers other than the main axial center.

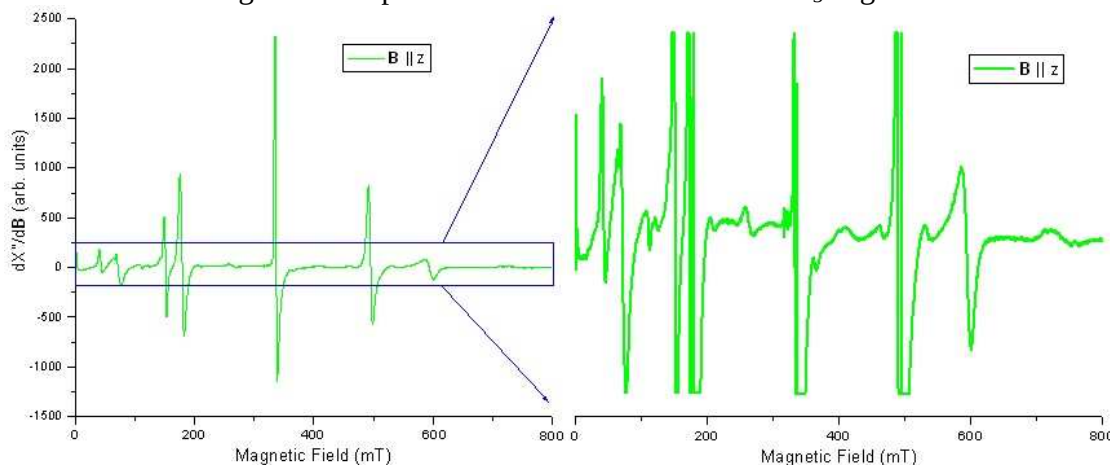
To confirm that the spectra from the stoichiometric sample could be used to aid in characterizing centers found in the congruent sample, Figure 22 on page 40 overlays both road maps. Note the similarity of many features, such as the non-axial behavior of

Figure 20 – Comparing EPR of Congruent and Stoichiometric LiNbO₃:Mg:Fe

The figure above shows a comparison between the spectra from the congruent and the stoichiometric LiNbO₃:Mg:Fe. The red spectra was also more intense, but this plot normalizes the data set so that the difference in width can be seen, most notable around 200 and 500 mT.

certain lines in the xy-plane, but also the many additional lines observed in the stoichiometric sample.

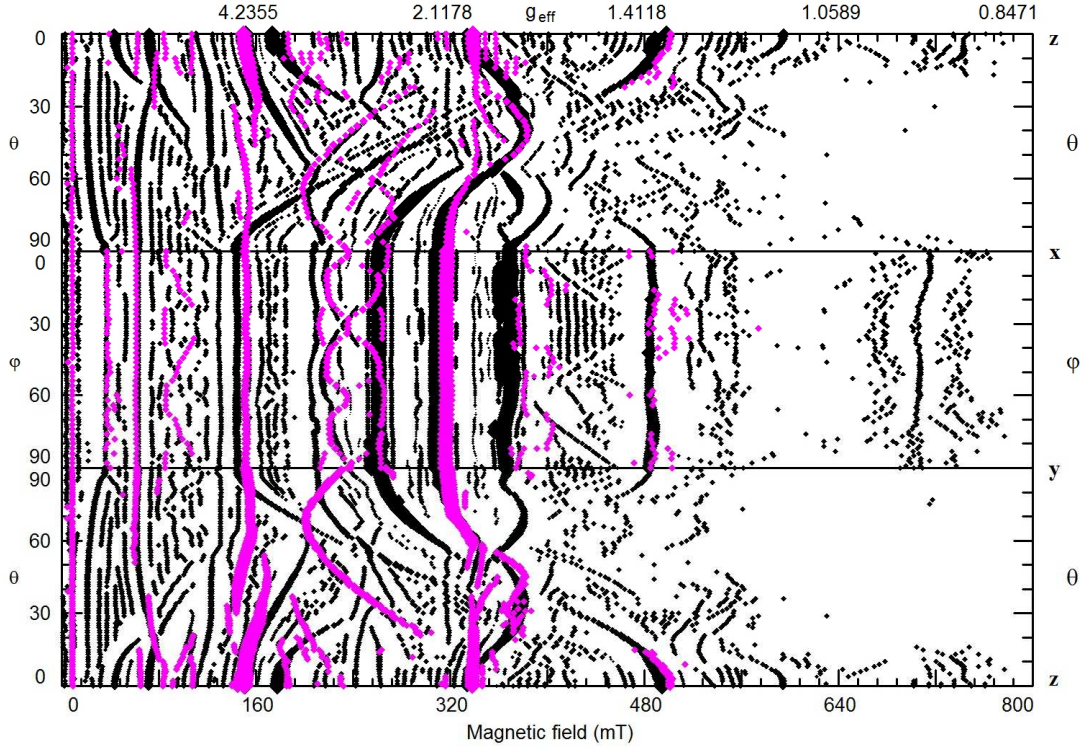
For fitting the data, the main axial center was first characterized approximately 40 years ago. This center is referred to as Fe1. There are also Fe3 and Fe4 observed in the stoichiometric sample, which are attributed to $\text{Fe}_{\text{Nb}}^{3+}$. It is not clear exactly what makes Fe3 different from Fe4. It is accepted that these centers occur due to the lack of charge compensators, and also compensate the main axial center.

Figure 21 – Spectra from Stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$ 

The figure above shows the entire spectrum on the left and a spectrum recorded using much higher gain for the same sample orientation. Note the abundance of small lines visible in between the large intensity lines.

Figures 23-27 on pages 41-44 show the experimental road map for the stoichiometric sample overlaid with calculated angular dependences for Fe1, Fe3 and Fe4. There is also a center known as Fe2 which was roughly studied several years ago, which appears when LiNbO_3 is codoped with Fe and Mg. It is accepted that Fe1, Fe 3 and F4 are axial centers of single Fe ions, but the nature of Fe2 is not so well known. The road map of the stoichiometric sample shows at least one non-axial center. This center is also entering congruent $\text{LiNbO}_3\text{:Mg:Fe}$, and is probably Fe2. The last figure also overlays all calculated angular dependencies for Fe1, Fe3 and Fe4 and has arrows to indicate lines belonging to at least one non-axial center.

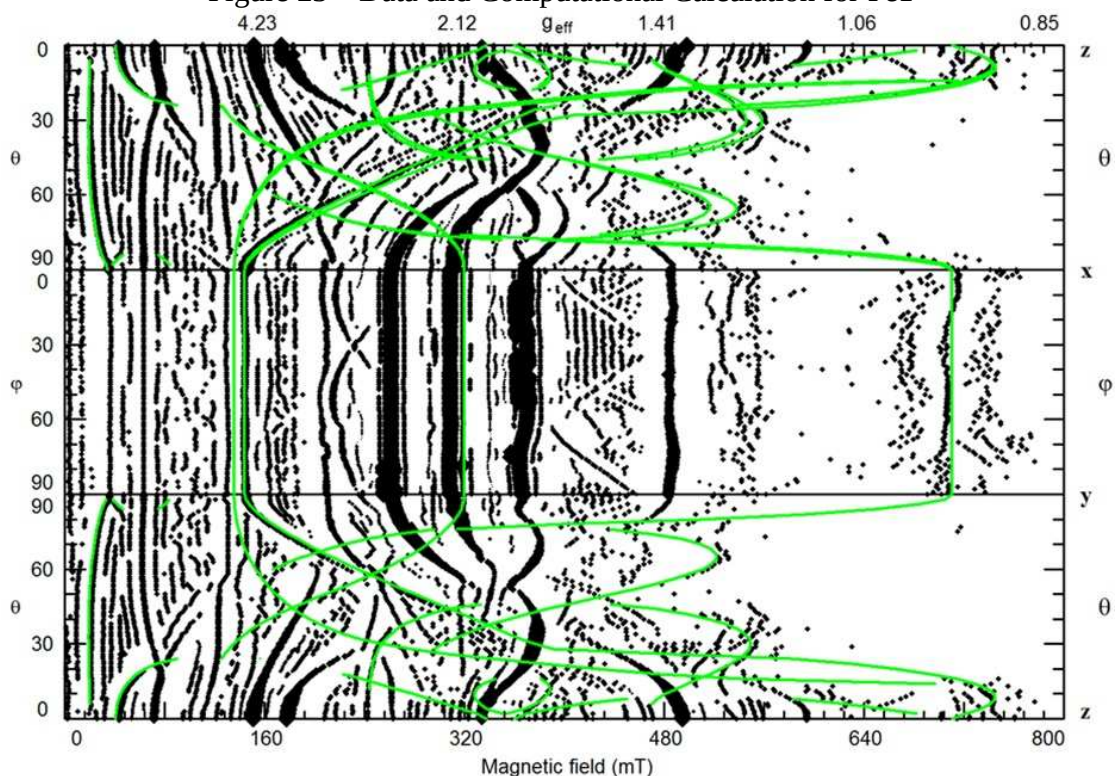
The lines highlighted with arrows above belong to at least one non-axial center. These could be explained by complexes of $\text{Fe}_{\text{Nb}}^{3+}$ with two $\text{Mg}_{\text{Li}}^{2+}$. This complex would completely compensate all charges. However, the analysis has not yet progressed to the point where this model can be proven.

Figure 22 – Overlay of Road Maps for Congruent and Stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$ 

The figure above shows the road map from the congruent material in magenta, and the road map from the stoichiometric material in black. Note that in the x-y plane, the non-axial lines observed in the congruent material match up well with the lines observed in the stoichiometric material.

Table 2 below displays parameters of the spin-Hamiltonian for axial Fe^{3+} centers Fe1, Fe3 and Fe4. Table 3 below displays a comparison of the values of axial crystal field b_2^0 parameter for several dopant centers, which can vary by surprising amounts depending on the ion's location.

Figure 23 – Data and Computational Calculation for Fe1



The above figure shows the data from stoichiometric LiNbO₃:Mg:Fe as well as a computational calculation of the angular dependence of Fe1, first observed over 40 years ago.

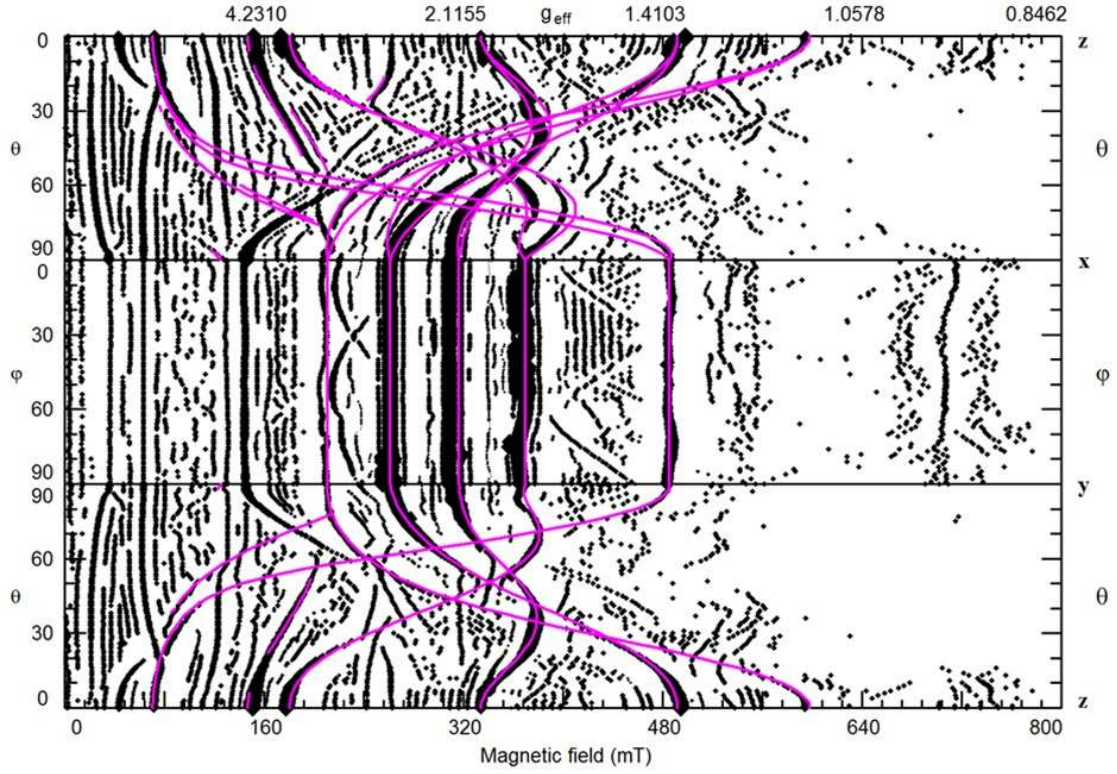
Table 2
Spin-Hamiltonian Parameters for Fe1, Fe2, Fe3

Center	Parameter					
	g_0^0	g_2^0	b_2^0	b_4^0	b_4^3	c_4^3
Fe1	1.995	0.012	1768	-49	± 650	-380
Fe3	2.005	-0.001	495	-59	± 1400	860
Fe4	2.004	-0.004	688	-41	± 420	380

Table 3
Comparison of the Axial Crystal Field Parameter b_2^0 for Several Centers

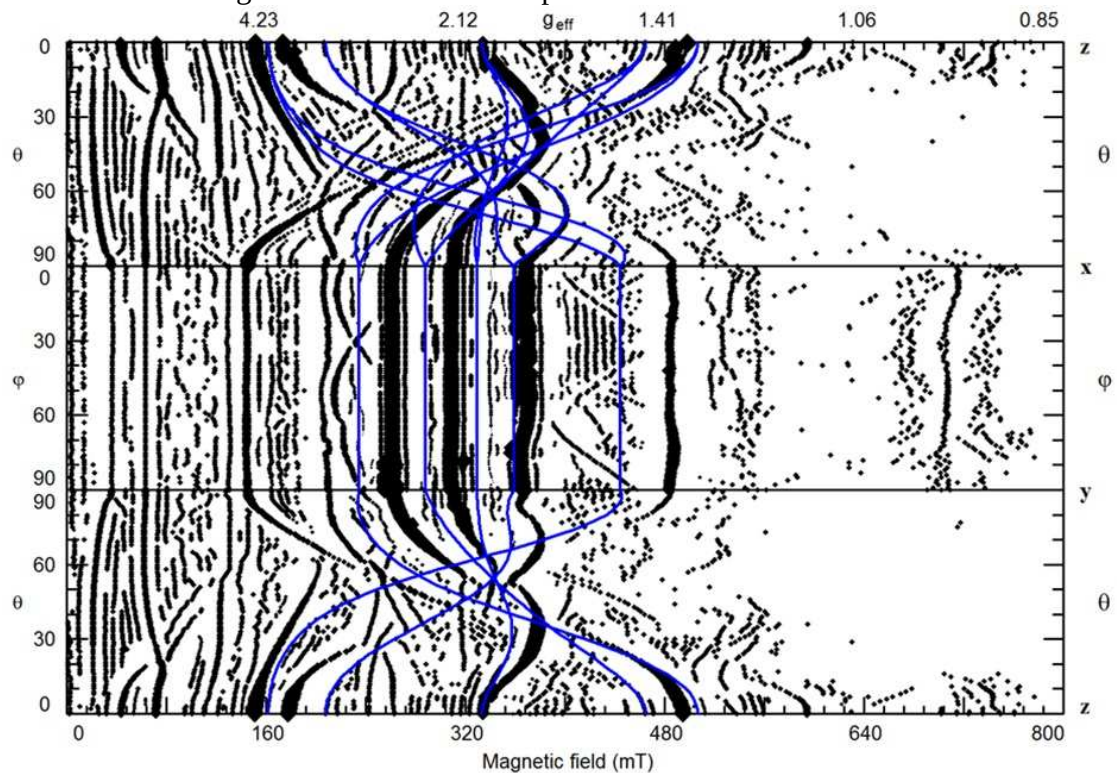
Crystal	Center					
	Mn _{Li}	Cr _{Li}	Cr _{Nb}	Fe _{Li}	Fe _{Nb}	Fe2
LiNbO ₃	0.088	-0.387	0.0215	+0.166	0.485	0.068
LiNbO ₃ :Mg			<0.01		0.042	<0.06

Figure 24 – Data and Computational Calculation for Fe3



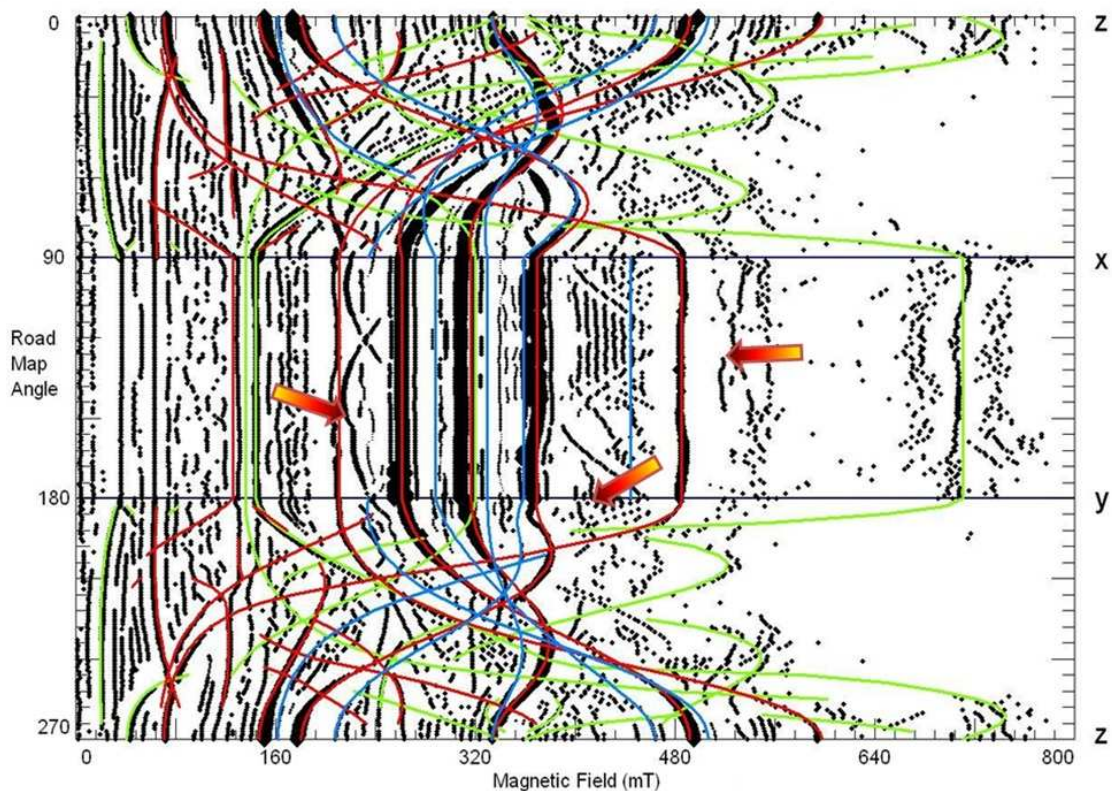
The above figure shows the data from stoichiometric LiNbO₃:Mg:Fe, as well as a computational calculation of the angular dependence of Fe³⁺, observed previously in stoichiometric LiNbO₃.

Figure 25 – Data and Computational Calculation for Fe4



The above figure shows the data from stoichiometric LiNbO₃:Mg:Fe as well as a computational calculation of the angular dependence of Fe⁴, observed previously in stoichiometric LiNbO₃.

Figure 26 – Data and All Calculations with Highlights for Non-Axial Center



The above figure shows the data from stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$ as well as all the computational calculations of angular dependences, Fe1 in green, Fe3 in red, and Fe4 in blue. This figure makes it easy to see that there are still some centers unaccounted for, most importantly at least one non-axial center, highlighted with arrows.

CONCLUSIONS

The structures of several centers in congruent lithium niobate heavily doped with chromium, congruent lithium niobate codoped with magnesium and iron, and finally stoichiometric lithium niobate codoped with magnesium and iron were investigated and characterized. These materials are important for use in industry; chromium was investigated for possible use in lasers, and iron was investigated for its photorefractive properties, particularly for possible holographic memory uses. Understanding how dopants enter the materials can have a useful impact, particularly for those applications requiring stoichiometric LiNbO_3 , where explaining the methods of charge compensation becomes more complicated.

The use of EPR to investigate these materials gave detailed information on several aspects of these dopant centers. In the heavily doped $\text{LiNbO}_3\text{:Cr}$, there were several lines attributed to chromium pair centers in addition to the main axial Cr^{3+} center. These centers had not been previously studied in detail. Since these centers exhibit an obvious angular dependence in the xy-plane, they must belong to low symmetry centers.

The initial model for the pairs as occupying Li and Nb nearest neighbor locations would produce an axial center, and so it cannot explain the experimental results. The most likely model of chromium pairs has both on Li sites does explain the angular dependence. This would require +4 charges for proper charge compensation. This can be explained by one Nb^{5+} vacancy, or 4 Li^+ vacancies. Since the linewidths of these centers are the same as for single Cr^{3+} centers, the option of 4 Li vacancies in the surrounding of the Cr-Cr pairs is less likely since these vacancies would be randomly

distributed around the center, and this would broaden the EPR lines.

In stoichiometric $\text{LiNbO}_3\text{:Mg:Fe}$, three axial centers and at least one non-axial center were identified. If there is a second non-axial center present, this would now be called Fe5. This was possible because: first the lack of charge compensators requires that they exist in the material in order for the desired concentrations of dopants to enter the material, and secondly because the lack of intrinsic defects gives better resolution and sensitivity for EPR lines. This analysis can help more accurately characterize Fe2 in congruent $\text{LiNbO}_3\text{:Mg:Fe}$.

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