Crystal Growth of Multiferroic Material Gadolinium Molybdate $Gd_2(MoO_4)_3$

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ABSRACT: At the NHMFL, we are growing β´-phase Gadolinium Molybdate crystals as part of a collaboration with the DeMille group at Yale to measure the electron electric dipole moment (EDM). The DeMille group at Yale is interested in the β´-phase Gadolinium Molybdate crystal because of it ferroelectric properties. Since the crystal is ferroelectric the electric dipole moments are all aligned causing it to be permanently electrically polarized. This β´-$Gd_2(MoO_4)_3$ crystal has a strong internal electric field which becomes even stronger upon cooling and because of this, Gadolinium Molybdate is a superior candidate for a future EDM experiment.

INTRODUCTION: In the exploration for new physics beyond the Standard model one route, the search for a permanent electric dipole moment (EDM) of elementary particles (i.e. electrons and neutrons), has become increasingly important and promising. An existence of a non-zero electric dipole moment would be evidence of both a violation of charge and parity symmetry (CP-violation) and time-reversal symmetry. The Standard Model predicts the EDM of the electron to be extremely small, d_e < 10 -40 e·cm, which is far beyond any current methods of detection. However, theoretical extension of the Standard Model like Supersymmetry and Grand Unification predict the EDM values of an electron to be within two orders of magnitude from the current EDM limits (1.6 x 10-27 e·cm). With the improvement in sensitivity of two orders of magnitudes or greater, evidence of new physics beyond the standard model could be excluded or even verified.

CRYSTAL STRUCTURE: The unit cell structure of β´-Gadolinium Molybdate is orthorhombic with unit cell parameters of a=10.392 Å, b=10.416 Å and c=10.696 Å. As seen in Figure 1, thin magnetic layers of Gadolinium separate layers of Molybdenum and Oxygen (Molybdates). The space symmetry group classification is Pba2, the point symmetry group is mm2. The blue tetrahedrons shapes of Molybdenum represent Molybdenum's bonds with the four surrounding Oxygen (at each point of the tetrahedron there is one oxygen atom).

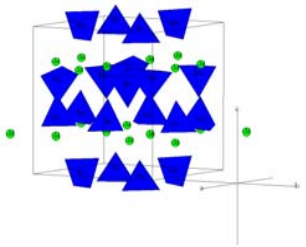


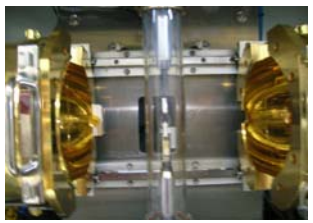
Figure 1: Unit cell of β´-$Gd_2(MoO_4)_3$

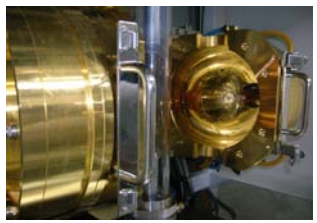
PROCEDURE: Powder rods of $Gd_2(MoO_4)_3$ were created using a solid state reaction method between Gd_2O_3 and MoO_3.

$$Gd_2O_3 + 3MoO_3 \rightarrow Gd_2(MoO_4)_3$$

To create a 5 gram homogenous powder rod, the material was fired twice in a furnace. The first firing was for 10 hours at 1000 °C and the second firing was for 11 hours at 1000 °C. In between the two firings the material was ground up to help produce a more homogeneous mixture of the two reactants. After the reaction was complete the $Gd_2(MoO_4)_3$ powder was compacted into a small, thin balloon at 25 psi to create a well formed rod.

Once the rod is formed, it is suspended in the middle of the image furnace between two gold-plated, concave reflective mirrors. At the vertex of each mirror is a powerful light bulb. Light emitted by the bulbs is focused at a point in the center of the sphere created by the two mirrors when they come together. Below the rod, a small aluminum cylinder is set in place to help maintain the stability of the liquid as it passes through the heated zone. Both rod and aluminum cylinder are slowly rotating in opposite directions and moving together down through the focal point of the two mirrors. While being dropped, small portions of the material are melted as they pass through the focal point and afterward cool to become a crystallized form of β´-$Gd_2(MoO_4)_3$. To ensure proper crystal growth the powder rod was pulled through the heated zone at 1cm/hour. The rotation speeds of the both the sample rod and aluminum cylinder were 25 rpm





Pictures 1 & 2: IF furnace with $Gd_2(MoO_4)_3$ rod inside the glass tube (left). Bulb at the vertex of gold-plated, concave reflective mirrors (right).

RESULTS: After about two weeks and three attempts we were successfully able to make a single crystal. Unfortunately the single crystal was extremely small and was insufficient for any experiments by itself. We then set about the next four weeks attempting to produce another single crystal.

This process proved to be very difficult and time consuming. When the rods are complete and ready to be placed in the image furnace they were usually a pure white color. Inside the image furnace the pure white surface of the $Gd_2(MoO_4)_3$ rod would reflect most of the light. Once the material started to melt in became black which created a huge temperature gradient between the liquid and solid portions of the rod. This proved to be the biggest obstacle in the crystallization process. Another obstacle we encountered was about 40 % of our rod samples, after coming out of the heating furnace, had a dirty yellow tint to them. Even though this property made the process of crystallization in the image furnace much easier, the final product turned out to be out poor quality.

After we were able to make enough of the β´-$Gd_2(MoO_4)_3$ crystal, the following test were preformed to confirm the properties of our sample.

Magnetic Susceptibility: The magnetic properties of $Gd_2(MoO_4)_3$ are due the Gd^{3+} ions, mainly the 7 electrons in the 4f orbital. The 4f orbital is much closer to the nucleus and therefore does not share in spin interaction with other electrons of neighboring atoms. Due to this characteristic of f orbitals, $Gd_2(MoO_4)_3$ remains paramagnetic down to very low temperatures (0.3K). The magnetization of our sample was measured using an applied magnetic field of 1000 G in a Superconducting Quantum Interference Device (SQUID). The data from this measurement confirms that the sample is indeed paramagnetic. Unfortunately we were only able reach temperatures down to approximately 1.7 K, and we were not able to observe any magnetic transition. Our data can be well described by the Curie-Weiss law, $\chi = C/(T - \theta_t)$, where C is the Curie constant, θ_t is the Curie point, and T is the temperature. From our graph we were able to calculate the specific Curie constant of the sample to be 7.69. This is very close to the accepted value of the Curie constant for Gd^{3+}, which is 7.88 [2].

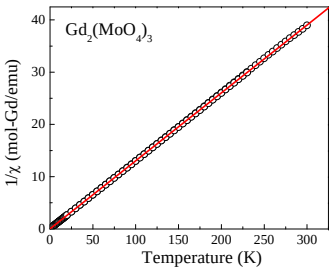
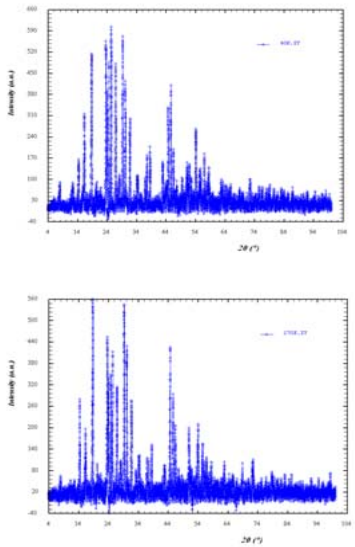


Figure 2: Temperature dependence of the inverse magnetic susceptibility for β´- Gd2(MoO4)3.

X-Ray Diffraction: According to G. Lucazeau and D. Machon [3] using Raman spectroscopy techniques, the β´-Gd2(MoO4)3 single crystal undergoes a small structural transition at 200 K. To confirm this and further study the transition, X-Diffraction test were preformed at 40 K and 270 K.

In the data taken from the X-ray diffraction changes in the intensity of the Bragg peaks were observed, indicating that a structural transition has occurred between 40 K and 270 K. Unfortunately, due to time constraints, we were not able to further investigate the structural transition. This will be done in the following weeks after the completion of the REU.



Figures 3 & 4: X-ray diffraction of β´-$Gd_2(MoO_4)_3$. sample at 40 K (above) and 270 K (below)

Future EDM experiment with Gadolinium Molybdate at Yale

INTRODUCTION: The Demille group at Yale University have identified the ferroelectric phase of Gadolinium Molybdate, β´-$Gd_2(MoO_4)_3$, as a prime candidate material in the search for the electron EDM. The intrinsic properties of Gadolinium Molybdate are able to give the high EDM sensitivity needed in such an experiment. The achievable limit of the electron EDM is given by the relationship

$$d_e = \frac{\mu_a}{\mu - 1}\frac{\delta B}{E_{eff}},$$

where μ_a is the magnetic moment of gadolinium, μ is the magnetic permeability of the material, E_{eff} is the effective electric field, and δB is the magnetic field sensitivity (a characteristic of the SQIUD). Gadolinium Molybdate is a ferroelectric material, and as a result an extremely large effective electric field is produced in a poled crystal, $E_{eff} \approx 20$ MV/cm. Gadolinium has a large atomic number, and the magnitude of the EDM grows by a factor that approximately follows as $\alpha^2 Z^3$. For Gadolinium this enhancement factor is ~ 14. The magnetic properties, due to the 4f electrons, of Gd^{3+} ions yields a magnetic permeability of μ -1= 0.3 at 4 K and the magnetic moment in the Gd^{3+} ions when a permanent EDM is induced is $\mu_a = 8\ \mu_B$, where μ_B is the Bohr magneton. The SQUID being used for this experiment is extremely sensitive and can achieve a magnetic field sensitivity of δB = 7 fT/√Hz. With all of these parameters and the use of the relationship above, the DeMille group at Yale projects the EDM sensitivity in this experiment to be $\mathbf{d_e \approx 3 \times 10^{-29}}$ **e·cm**. This limit is a two order of magnitude improvement on the current standing limit, and if this degree of sensitivity can be achieved then a number of theories beyond the Standard Model can be explored further or ruled out.

EXPERIMENTAL SETUP: For a spin-1/2 particle, an EDM must point along the magnetic moment of the particle. When an electric field is applied to the sample, it will orientate permanent electric dipole moments along the field. This in turn will orientate the magnetic moments also, creating magnetization. Using a SQUID magnetometer, this magnetization can be detected as the electric field is reversed. As seen in Figure 5, an applied voltage will run across the material, orientating both electric and magnetic dipole moment. The applied voltage will then be reversed, causing both moments to flip. This flip will induce a current in the pick up loop that is then detected in the input coil. This setup will be cooled to 4 K so the effective electric field inside the crystal can be large.

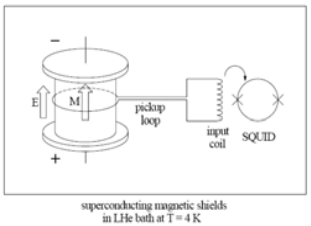


Figure 5: Experimental setup for EDM experiment.

CONCLUSION: After six weeks of attempts, we were finally able to make a high quality β´-$Gd_2(MoO_4)_3$ crystal. An through the testing of magnetic susceptibility and X-ray diffraction we were able to confirm the final product. There are a few more test that need to be done in preparation before sending the single crystal to the Demille group at Yale. One of the main properties we were not able to test, due to time constraints, was the electric susceptibility of the single crystal. Fortunately, these test will take place in the following weeks after the REU is finished.

AKNOWLEGDEMENTS: Through this REU I have learned so much and I am truly appreciative for all the help given to me. I would like to thank Dr. Wiebe for his guidance in the past two months and Haidong Zhou for all the help in the lab. Thanks to Jose Sanchez and Pat Dixon in the CIRL/REU office for letting me be a part of this experience and The National Science Foundation NSF for funding the NHMFL REU.

References:

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