Nuclear relaxation in CoGa$_3$ lattice structures

by

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January 2010
Foreword

This is a research report written by Prastuti Singh that describes research carried out by her in the Collins research group in the Summer and Fall of 2009. The research was part of a culminating senior project that she completed for a high school degree at Pullman High School, Pullman, Washington.

Prastuti wrote the report and submitted it to the highly competitive *Intel Science Talent Search* in November 2009. She was selected as a semifinalist in January 2010, winning not only that honor but a $1000 personal prize as well as a similar prize for Pullman High School. In March 2010, while still a high school student, she entered a university-wide poster competition at Washington State University. Below is a photo of her at the event. As of this writing, Prasuti is majoring in physics at Caltech.

The research described herein was supported in part by the National Science Foundation under grant DMR 09-04096 (Metals Program).

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October 2012
Nuclear Relaxation in CoGa$_3$ Lattice Structures

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June 2009-
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Perturbed Angular Correlation (PAC) Spectroscopy is a method utilized to study hyperfine interactions within solids by observing the gamma rays emitted by the nuclear decay of probe atoms that have been artificially infused into the crystal structure. The $^{111}$In is a highly advantageous probe atom to use because its intermediate stage, $^{111}$Cd, is relatively long lived and therefore provides researchers ample time to observe interactions. The purpose behind studying these hyperfine interactions is to gain a better understanding of atom diffusion in solids, whose properties (such as magnetic or electrical) often depend upon the distribution of atoms/elements. Through PAC, one can gain a better understanding of solids and their uses. The specific purpose of this project was to investigate the crystals of the CoGa$_3$ structure and observe changes across different crystals. Samples were prepared using an arc furnace and then placed into the PAC to run for 6-10 (sometimes longer) days. CoGa$_3$ structures contain two Ga (or In as the case might be) sites so two signals were expected and received. The curious aspect of the research was the relaxation frequency. The In$_3$Rh and In$_3$Ru seem to have a relaxation frequency crossover between the two sites while the In$_3$Ir contained a shift from one iridium boundary to the other. The reason behind these occurrences is probably caused by the change in composition over time as the $^{111}$In decays.
Introduction

Perturbed Angular Correlation (PAC) Spectroscopy is a method used to study hyperfine interactions within solids by observing gamma rays emitted by the nuclear decay of probe atoms from the solid. Part of the theory behind PAC was developed by D. R. Hamilton in the 1940s. His paper outlined a method one could theoretically use to determine gamma-gamma correlation. It was seven years before anyone managed to observe such a correlation. E. L. Brady and M. Deutsch were able to successfully discern a signal and correlation using Geiger counters (very primitive given their low gamma detection capabilities and almost no time resolution at all) [1].

It was Hans Frauenfelder, who is credited with the invention of the PAC Spectroscopy method in 1951. Frauenfelder was a Swiss scientist who received his graduated degree from the Swiss Federal Institute of Technology under Paul Scherrer and was taught by the likes of Wolfgang Pauli. Using a scintillation detector, gamma-gamma correlation became the standard for determining nuclear spins and parities [2]. (A scintillation detector consists of a scintillator, a luminescent material that absorbs the energy of an incoming particle and then reemits it as a flash of light, and generally a photomultiplier tube, which absorbs the light emitted by the scintillator and then proceeds to reemit it as an electron. The electrons can then be examined to gather information about the original particle [3]).

Comparable methods include the more widely known Mossbauer Effect and Nuclear Magnetic Resonance (NMR). PAC is more effective than these because it allows for measurements to be made at higher temperatures. In the other two effects, signals become damped at high temperatures because of Boltzmann effect. PAC is limited though in its experimental methods. Only very specific probe atoms can be used because of nuclear requirements [4].

PAC is neither a widely known nor a widely used method. Dr. Gary Collins' laboratory in Pullman, Washington is the only location in the United States it is used. There are several locations in Europe and Asia where research is currently being conducted. The purpose of the work at Dr. Collins’ laboratory is to essentially seek a deeper understanding of atom diffusion in solids. Many properties of solids such as magnetic or optical is dependent upon how elements are distributed so through this research one hopes to gain a better understanding of how solids behave. In the future, these solids could be used for developments in electronics or energy efficiency [5].

The focus of this specific experiment was originally to study more systems with the highly unusual and complicated CoGa$_3$ structure. CoGa$_3$ has a tetragonal structure with two inequivalent Ga sites in the 2:1 ratio. The Ga1 site consists of Ga atoms centered in cubes of Ga2 site atoms. The Co atoms are in the alternating rhombic spaces. Assuming there are no atoms jumping from one site to the other, the Ga1 site atoms must jump from one center to another while the Ga2 site atoms can jump to another space on the Ga2 lattice relatively easily [6].
The purpose of this experiment is to determine whether this proposed structure for CoGa₃ and a few others crystals hypothesized to have this structure. If they do indeed have this structure, the next goal would be to compare and contrast the crystals and diffusion of the $^{111}$In probe across them.

**Explanation**

The first step in the procedure is the sample preparation. But before the sample can be made, a target composition is decided upon. To form In₃Rh, for example, the percent composition of In needs to be approximately 75%. The target compositions would then be either In rich (>75% In composition) or In poor (<75% In composition) [7]. If this weren’t an indide (In compound), the In probe atoms would sit on the poor lattice structure. So if the target was In rich, there would be spaces on the Rh lattice structure for the In probe atoms. But since most of the compounds used in this experiment were indides, most of the In probe atoms are expected to settle on the In lattice structure. The composition targeting is a method of extending control over the experiment. Generally, samples are made at both the rich and poor boundary to check for any differences.

Once the boundary has been decided upon, the sample can be made. Depending on the percent composition target, determine the mass of the two samples needed. The total mass of the sample should be between 50 to 100 g [7]. Samples of the elements are then cut, cleaned with deionized water, and weighed. Be sure to use gloves at all times and the equipment marked with radioactive symbols only once the $^{111}$In has been used.

The probe atoms were artificially infused into the crystal structure during the experimental preparation process. $^{111}$In is the most commonly used probe atom because it decays into $^{111}$Cd, which has a relatively long life, allowing researchers enough time to carefully observe the crystal structure and how the $^{111}$In has diffused into the structure. The $^{111}$In is in liquid form and highly radioactive so it is necessary to be extremely careful when working with it. Using a dropper, drop either 2-3 drops of $^{111}$In onto the larger sheet of element. Measure the activity and if it is near 3000 Mrad, place the sample under the fume hood to dry for approximately 2 hours. The indides nearly always took more time. It was difficult to tell sometimes whether the $^{111}$In had actually dried or not. After the sample looks sufficiently dry, take count of the activity again. Make sure it is approximately 1500 Mrad. If it is not, add more $^{111}$In and dry the sample once again. If it is more, proceed.
Use an arc furnace to melt the sample. An arc furnace is a furnace used to prepare metallic alloys by melting them by means of an electric arc under flowing argon gas. It uses a tungsten cathode and a welder's power supply [7] to create an arc with a current of the order of 45 amps in order to melt the samples. Begin by taking two Q-tips and cleaning the arc furnace’s base with NO and place the sample in the middle of the cleaned area. Then close up the furnace by screwing the shield in place. Let the argon flow for approximately ten minutes. After that, you are ready to begin using the arc furnace. Set the power supply to 45 amps and put on the protective mask. Bring the electrode down towards the base plate and slowly touch the place and lift, forming an arc. Move the arc towards the sample until the arc jumps from the electrode to the sample. When the arc jumps, the sample melts. The sample should have melted immediately so poke and move it around with the electrode to check the sample. It should have a circular shape. If not, try melting again however melting too many times will reduce the amount of radiation.

After the sample has been melted, shut off the argon flow and wait for another ten minutes. Unscrew the shield and remove the sample. Weigh it and take count of the activity. Record in the lab notebook. Calculate error using mass loss and assuming one sample lost all the mass and then the other. Close up the lab, disposing of all radioactive materials (such as gloves) appropriately.

The next part of the experiment involves using the PAC Spectrometer to collect data. The PAC consists of four BaF$_2$ scintillation detectors placed at 90° angles around a central oven. Two of the detectors detect the start of the gamma ray signal formation while the other two observe the end of the signal. A start and a stop signal are always placed across from each other. A clock is used to record the time interval between the start and the stop. From this data, a perturbation function, $G_2(t)$ can be made, which is actually the time spectra that one fits using SmartTerm [5].

In the work room, lower the temperature on the PAC to less than 15°C. Once the temperature has dropped, turn off the vacuum pump and wait for the pressure to drop. Once the pressure has dropped below a specific mark (changes depending on which PAC is being used—generally in the order of 10$^5$), remove the bolts from the cover and slowly lift it. Remove the molybdenum heat shield and the previous sample, placing it in its labeled container. Place the new sample into the oven and cover with the heat shield and then the coiled exterior cover. Screw the bolts back in and then turn the vacuum pump on. Once the pressure is sufficiently high, increase the temperature to 400°C (this initial value for the temperature depends upon the sample but for the CoGa$_3$ samples, the starting temperature was 400°C each time). Wait for the temperature to increase to the set temperature. Once it has, start the data collection program on the computer.

For the next week or so (until the sample becomes too weak—explained later), come in each day and save the previous day’s data on the data collection program. After saving, fit the data using SmartTerm Office. Print off a data summary sheet, a Fourier transform and a time spectra. The fitting programs for the last two are ‘fft’ and ‘fit10’. Other steps in the procedure are self-explanatory for the most part. The program asks specific question and basic knowledge of FORTRAN computer language is required to answer them. Fit an $a_0$ (begin with setting it at 0.2), the site fractions $f_1$ and $f_2$ (0.4 and 0.2), $\omega_1$ and $\omega_2$, eta1, and lam1 and lam2 if there is evidence of any relaxation. Determine $\omega_1$ and $\omega_2$ from the Fourier Transform. $\omega_1$ is the value of the first signal and $\omega_2$ is the value of the second harmonic on that signal. Each signal consists of three peaks and they are generally either in the ratio 1:2:3 or 5:8:13 [7]. For the CoGa$_3$ samples, the first harmonic (peaks) of both signals are at the same location i.e. they have the same value. So the large
Signal is \( \omega_1 \) and the subsequent one is \( \omega_2 \). \( \text{Eta} \) is defined as \( 2 - \frac{w_2}{w_1} \) [7]. Relaxation for the first time is mainly determined by looking at the time spectra and seeing if any of the signals are damping. Use the command 0 for fixing values and 1 for fitting them. The Chi2 value is a measurement of how close the data is fitted. Values closer to 1 indicate good fits.

\( a_0 \) will increase each day as it is inversely proportional to the amount of activity left in the sample. Once the \( a_0 \) becomes too large (>0.6 or so) and other values start deviating from what they should be, the sample can be considered dead. Stop data collection at that point.

After the data has been fitted, change the temperature on the PAC and start the next run. From 400°C, increase by 100°C each day until the signals on the Fourier transform become murky (around 700°C). At that point, decrease by 50°C to fill in the gaps between and the other data points and then the 25 and 75°C marks. Once the sample looks like it is weak, run at higher temperatures such as 725°C or 700°C again. This is just one possibility of a series to follow. Each sample is different and therefore, the order of the temperatures is different. This model generally works however.

Analyze the data each day, looking for changes from one day to the next in the values. For the CoGa3 samples, \( \omega_1 \) and \( \omega_2 \) stayed the same throughout the run for the most part at about 343 Hz and 332 Hz.

Once the runs have been completed, the relaxation frequencies can be used to determine an activation energy for the jump at each In site.

\( \text{In}_3\text{Rh} \) was the first sample to be made, followed by \( \text{In}_3\text{Ir} \). Towards the end, \( \text{In}_3\text{Ru} \) was made. The first \( \text{In}_3\text{Ru} \) sample was defective however. The ruthenium was in powder form and very difficult to work with. The sample didn’t turn out well.

**Results**

Example time spectra and Fourier transform attached (pg 6 and 7). Data of sample \( \text{In}_3\text{Rh} \) 27.2%Rh (22.4-28.7% Rh error) at 575°C. The chi2 is 1.083 so it is a very good fit. The damping values, \( \lambda m_1 \) and \( \lambda m_2 \), were 5.71 MHz (±0.767) and 0.712 MHz (±0.717) respectively. These are relatively small damping factors, especially \( \lambda m_2 \), but the damping is still visible in the time spectra. The two different signals are also visible, one larger than the other. For the \( \text{In}_3\text{Ir} \), data at eight different temperatures was used. There were several other days of data but they were towards the end and their behavior was erratic. It was decided those values were not be used.

Damping might not immediately be visible in the Fourier transform. Two or more days of data are generally required to observe damping. The jump frequencies are visible however. The three peaks marked in blue are in the approximate ratio 1:2:3 (330:650:960). The 1:2:3 ratio is indicative of a highly asymmetric EFG (electric field gradient) at the site while the 5:8:13 is indicative of axial symmetry. The 1:2:3 ratios are on In2 site whereas the 5:8:13 is of the In1 site. \( \lambda m_1 \) is the relaxation frequency at the In2 site and \( \lambda m_2 \) is at the In1 site.
The In$_2$Co sample did not turn out as expected. About halfway through the run, the sample's jump and relaxation frequencies underwent a dramatic change and the signals on the time spectra changed as well.

The graph shows a time spectrum with frequency on the x-axis and amplitude on the y-axis. The spectrum exhibits a series of oscillations with varying amplitudes.

Reduction parameters:
- **PACS30A**: Fit to 7 quadrupole, PE Plot = 5021544, Calib = 0.9600
- **Chi^2** = 1.000 / 993, Fit = 524102020201524, Tmin/max = -500.00 500.00
- A0: 0.44324, -0.30408E-02, 50 LAM2 = 0.71223, 0.71740
- A1: -0.97740E-04, 0.16535E-04, 70 P1 = 1.5000, 0.00000E+00
- F1: 0.23073, -0.17303E-01, 71 P2 = 1.5000, 0.00000E+00
- F2: 0.11718, 0.12609E-01, 72 P3 = 1.5000, 0.00000E+00
- W1: 334.95, -0.77378, 73 P4 = 1.5000, 0.00000E+00
- K2: 325.75, -0.74470, 74 P5 = 1.5000, 0.00000E+00
- ETA1: 0.56860, -0.25560E-02, 75 P6 = 1.5000, 0.00000E+00
- ETA2: -0.18073E-02, 0.32776E-02, 76 P7 = 1.5000, 0.00000E+00

Redo##
Fourier AMPLITUDE Spectrum: 0.00 to 1200.00 Mrad/sec
TUKEY-HANNING (COSINE) WINDOW
MAX FFT AMPLITUDE = 0.419232
TIME DOMAIN: CH. 600 to 1448
TIME CAL = 0.950000 ns/ch
FREQ. CAL = 3.19579 Mrad/s/ch
LEGENDRE POLYNOMIAL OF DEGREE -1 SUBTRACTED
In$_3$Ir had a very peculiar behavior. About halfway through the run, the jump frequencies shifted upwards (graphs in Discussion).

The In$_3$Ru was a difficult sample to make and arc melting it actually required 55 amps because of ruthenium's high melting temperature. The data itself shows the In3Ru sample to be very similar to the In$_3$Rh sample.

Discussion

Overall, the results from this research project were unexpected, to say the least. I was anticipating similar behavior across all the samples since they have the same crystal structure with slight differences in the numerical data to account for the different elements used along with the indium.

As stated in the results above, the In$_3$Co experienced a dramatic change in its behavior. The jump frequencies changed from approximately 330 Mrad/s to 243 Mrad/s. Such a change normally does not occur in samples. It was later concluded sample had actually transformed from In$_3$Co to In$_2$Co. While is an uncommon occurrence, it is not impossible. With only three to four days of data for In$_3$Co and In$_2$Co, very little quantitative information can be gleamed.

The In$_3$Rh sample (made at the Rh rich boundary) had a very successful run. The jump frequencies were 330 Mrad/s and 320 Mrad/s for the entire run. Towards the end, a third signal of 120 Mrad/s was observed but it was determined to be a junk signal because there is no physical basis for the signal and it was inscrutable on the time spectra. The main interest in this sample (and the ones that followed) was the relaxation of the frequencies. In the series of time spectras shown (pg 9), the damping or relaxation is clearly visible from 500°C to 750°C.

Evidence of damping is visible in the Fourier transforms as well (pg). The broadening of the peaks across the same temperature range indicates damping [5].
The graph shows the function $G_2(t)$ for different temperatures: 750°C, 700°C, 650°C, 600°C, and 500°C. The x-axis represents time in nanoseconds ($t [\text{ns}]$) ranging from -200 to 200, and the y-axis represents the function values ranging from 0 to 1.
The following graph plots the relaxation \((\text{lam})\) vs \(1/k_B T\) where \(k_B\) is Boltzmann's constant. The y-axis is on a logarithmic scale. The open triangles are data from the In2 site while the closed triangles are data from the In1 site. There is very clearly a meeting of the relaxation on the two sites at about 750°C (1023 K). In this graph, there seems to be a crossover but of course, since there are no data points after 750°C, the two lines or relaxation frequencies could start acting as one because of the high temperatures. The muddied signals on the Fourier transforms make it difficult to run samples at temperatures beyond 750°C.

Assuming this relaxation is a crossover, one can determine the activation energy at each site, which is actually just the slope of the two best fit lines drawn. The equation to use is \(w = w_0 e^{-Q/(k_B T)}\), where \(w\) is the jump frequency and \(w_0\) is a jump frequency pre-factor (jump frequency at infinite temperature). \(T\) is clearly temperature and \(Q\) is the activation energy [5]. The program FIT10 on SmartTerm Office can be used to fit that data to this function. The process of fitting is too lengthy to mention but essentially, make a data set using 'eve' and then run FIT10 and fit as done while initially fitting the raw data.

For this sample of In3Rh, the fitting program yielded an activation energy of 1.24 eV on the In1 site and an activation energy of 0.934 eV on the In2 site, indicating the eVs required for an atom to jump onto each site. The In3Rh sample made at the opposite boundary exhibited similar behavior.
The next sample to be made was In$_3$Ir, which was expected to show behavior similar to the In$_3$Ir. Instead there was a shift, as mentioned above. Since the shift occurred halfway through the run and was not affected by the temperature, the cause is In evaporation in the sample. The In$_3$Ir shifted boundaries from being In rich initially to In poor. When the sample In$_3$Ir at the poor boundary ran in the PAC, the data corroborated that hypothesis. This shift is visible in the next few graphs. The grey data points are from after the shift and the black and white are from before the shift. The In$_2$ site from the initial set of data points matches up almost directly with the In$_1$ site from the data taken after the shift.

The activation energies also match. Before the switch, the activation energies were 1.271 (±0.0967) eV and 0.9418 (±0.1248) eV on the In$_1$ site and In$_2$ site respectively. After the switch, the activation energies were 0.9645 (±0.1041) eV on the In$_1$ site and 0.6241 (±0.0441) eV on the In$_2$ site. The energies for the In$_2$ site before the switch and the In$_1$ site after the switch are extremely close. They differ by approximately 2.5% and fall within each other's error ranges. This data further supports the above hypothesis.
The In$_3$Ru sample runs are not complete but from the data so far, it seems very similar to the In$_3$Rh sample. There seems to be a crossover at approximately the same temperature, 750°C, as In$_3$Rh, if not slightly higher because of ruthenium’s higher melting temperature.

The data does support the crystal structure hypothesized for CoGa$_3$ and others. There are two signals observed by the scintillation detectors and visible on the time spectra and Fourier transform. These two signals are indicative of the two jumps taking place as the $^{111}$In decays.

Comparing the data from the samples shows similar jump frequencies, approximately 330 MHz on the In1 site and 320 on the In2 site. This is not entirely unexpected since all the crystals possess the same structure but the differing relaxation patterns were a surprise. The In$_3$Rh and In$_3$Ru seem to be similar but the In$_3$Ir is completely different. Both the crossover and the shift observed are unusual and hardly ever seen. The shift, at least, seems to be a result of composition. As the In decays, the structure changes boundaries. The reason for the crossover is unclear but it is possibility it is a result of composition as well. As the In decays, the jumps could increase in speed and the gap between the two sites could close, which would support not necessarily a crossover but more of a melding of the relaxation frequencies. In support of a crossover, it could be possible that most of the $^{111}$In settled on the In2 sites so as it decays, jumps become easier on the In2 site and more difficult on the In1 site.
Bibliographical References


