Improved modelling of magnetic splitting in a chrome alum below 300 mK

C Gunderson\textsuperscript{1}, F Miller\textsuperscript{1}, T Chui\textsuperscript{2}, C Paine\textsuperscript{2}, T Prouve\textsuperscript{2} and W Holmes\textsuperscript{2}

\textsuperscript{1}Department of Engineering, University of Wisconsin, Madison, USA
\textsuperscript{2}Jet Propulsion Laboratory, California Institute of Technology, Pasadena, USA

E-mail: cmgunderson@wisc.edu

Abstract. Chrome-Caesium Alum (CCA) is a paramagnetic salt that can be used to achieve ultra-low temperature refrigeration through adiabatic demagnetization. Cooling capacity measurements of CCA show a significant reduction below the isolated paramagnetic spin model for temperatures below 100 mK. A more complete understanding of the thermodynamic properties of CCA could improve model accuracy, vital for meeting cooling requirements at sub-Kelvin temperatures. Modelling effort was undertaken to understand the physical origin of this reduction in heat and refrigeration capacity, and measurements from two separate CCA salt pills between 50 mK and 300 mK were used for model validation. Both the model and the experimental design and results are discussed in this work. The model uses exact eigenvalues for the Cr\textsuperscript{3+} ions from the spin Hamiltonian. Two interactions of interest are the zero-field splitting and hyperfine splitting, as these are not standard in presently used models.

We found that, though hyperfine interactions were not significant at temperatures above 50 mK, the inclusion of the zero-field splitting interaction resulted in qualitative agreement with the data. We optimized this model using a nonlinear least square regression to find the best fit to the two experimental data sets with two independent fitting parameters. Measured data at 50 mK still show a significant reduction below the fitted model prediction. Conductance measurements and thermal relaxation times were used to characterize addenda heat capacity and entropy loss due to non-adiabatic effects, which were not found to be significant. Accordingly, cooling capacity reduction below 50 mK cannot be accounted for by these effects. CCA is in the same chemical family as Chrome-Potassium Alum (CPA) which used widely in adiabatic demagnetization refrigerators. Thus, this modelling work described here is applicable to CPA. New measurements are planned to understand if the remaining discrepancy between the model and data is a systematic effect or a more fundamental feature of the salt.

1. Introduction

Sub-Kelvin cooling is essential for maximizing the sensitivity of detectors used in far-IR, millimetre, and X-ray astrophysics missions. Adiabatic demagnetization of paramagnetic salt pills can be used to achieve ultra-low temperatures and provide the necessary cryogenic refrigeration \cite{1, 2}. A thorough understanding of the magnetic heat capacity of these salts approaching zero Kelvin is vital to designing systems that meet instrument cooling requirements. Current thermodynamic models are in poor agreement with experimental data in this range however, as the magnetic behaviour becomes complicated by energy splitting due to the crystalline electric field, spin-orbit coupling, dipole-dipole interactions, and exchange interactions \cite{3, 4}. More specifically, cooling capacity measurements of Chrome-Caesium Alum (CCA) show a significant reduction below the isolated paramagnetic spin model for temperatures below 100 mK, likely due in part to omitted low temperature effects. In an effort to
better understand the low-temperature behaviour and effects of select interactions, we use a magnetic spin Hamiltonian to predict the paramagnetic properties of CCA and discuss the validity of this model through comparison with experimental results from two separate salt pills with data taken between 50 mK and 300 mK. Though the modelling effort described in this paper focuses on a single alum, CCA, similar energy splittings are seen in other alums. Ferric Ammonium Alum (FAA) and Chrome-Potassium Alum (CPA), for instance, are both widely used in adiabatic demagnetization refrigerators and exhibit heat capacity anomalies similar to CCA approaching zero Kelvin. An improved understanding of the thermodynamic behaviour of CCA would therefore enable enhanced modelling of other alums as well.

2. Background

2.1. CCA chemical formula and paramagnetic properties
As previously noted, CCA is part of the alum chemical family. Alums are a group of hydrated double salts with the formula:

\[ \text{R}^+\text{R}^{iii}(\text{R}^{vi}\text{O}_x)_2 \cdot 12\text{H}_2\text{O} \]  

where \( \text{R}^+ \) is a monovalent cation, \( \text{R}^{iii} \) is a trivalent cation, and \( \text{R}^{vi} \) is Sulphur for the case considered [5]. In CCA, the monovalent ion is Cs\(^+\) and the trivalent ion is Cr\(^{3+}\). Cr\(^{3+}\) is in the transition group and gives CCA its paramagnetic properties due to electrons in its unfilled 3d shell [4]. These unpaired electrons create a magnetic moment in the ion and result in a nonzero spin value of \( S=3/2 \). Additionally, approximately 9.5% of the Cr\(^{3+}\) ions have a nonzero nuclear spin of \( I=3/2 \). Further information on stable Cr\(^{3+}\) isotopes is given in table 1 [6]. The alum crystal is composed of face-centred cubic unit cells, each containing four trivalent ions [4]. Every trivalent ion is surrounded by an octahedron of six water molecules, creating near cubic crystal electric field symmetry at the ion and lowering the electrostatic energy of the \( d_\epsilon \) orbitals (xy, yz, and zx) relative to the \( d_\gamma \) orbitals (\( x^2-y^2 \) and 2\( z^2-x^2-y^2 \)) [4]. With just three electrons in the 3d shell in Cr\(^{3+}\), this energy shift results in a half-filled \( d_\epsilon \) triplet and effectively quenches the orbital momentum [4, 7].

| Isotope | S Spin | I Spin | Abundance |
|---------|--------|--------|-----------|
| Cr\(^{50}\) | 3/2 | 0 | 0.0435 |
| Cr\(^{52}\) | 3/2 | 0 | 0.8379 |
| Cr\(^{53}\) | 3/2 | 3/2 | 0.0950 |
| Cr\(^{54}\) | 3/2 | 0 | 0.0237 |

2.2. Zero field splitting
Distortions in the octahedrons can result in additional trigonal splitting, in which case the four trivalent ions in the unit cell are no longer equivalent and the direction of the external field relative to the crystalline axes needs to be considered [7]. For trigonal splitting, these symmetry axes are approximately oriented along each of the four cell body diagonals [8]. Though the trigonal field does not have a direct effect on the ground state, it gives rise to a spin-orbital coupling between the ground \( ^4S_{3/2} \) state and \( ^4P_{3/2} \) state that can split the ground state levels by a few tenths of a cm\(^{-1} \) [7, 9]. The total resulting change to the energy levels due to the crystal electric field is known as Zero Field Splitting (ZFS).

2.3. Zeeman splitting
When paramagnetic salts are placed in external magnetic fields, the interactions between the electron magnetic moments and the external field further split the energy levels of the ground state through the Zeeman effect. The combined ZFS and Zeeman effects for a Cr\(^{3+}\) ion in a trigonally distorted octahedron are shown in figure 1, where the Zeeman effect is qualitatively shown as a function of increasing applied field for the energy levels in the ground state [9]. In predicting the thermodynamic behaviour of these
ions only the ground state needs to be considered [8]. The relevant energy levels are magnified in figure 1.

![Energy vs Magnetic Field](image)

**Figure 1.** Explanation of energy splitting in ground state of Cr$^{3+}$ ion in trigonally distorted octahedron [8]. Relevant energy levels are shown in the magnified graph on the right.

### 2.4. Hyperfine splitting
Lastly, as reported in table 1, Cr$^{3+}$ has a stable isotope with nonzero nuclear spin: Cr$^{53}$ with I=3/2. In this case, the nuclear magnetic moment interacts with the electronic magnetic moment, subdividing each electronic energy level [4]. The unpaired electrons in the ion can also create an electric field gradient at the nucleus, consequently making some orientations of the nuclear quadrupole moment more favourable than others, further splitting the energy levels [4]. One final consideration is the interaction between an externally applied field and the nuclear magnetic moment, which is analogous to, but far smaller than, the electronic Zeeman effect. Though the nonzero nuclear spin isotope of Cr$^{3+}$ has a relative natural abundance of just 9.5%, the associated hyperfine interaction terms that arise from a positive nuclear spin have been included in this analysis for completeness.

### 3. Model

#### 3.1. Magnetic spin Hamiltonian
Together, the above-mentioned interactions comprise the magnetic spin Hamiltonian for a paramagnetic ion in a crystal, which can generally predict the behaviour of the lowest energy levels. The Hamiltonian, assuming axial symmetry, is given as [4, 10, 9]:

$$
\mathcal{H} = \beta g H S_z + \beta g_1 (H_x S_x + H_y S_y) + D \left( S_z^2 - \frac{1}{3} S(S+1) \right) + A S_z I_z + B \left( S_x I_x + S_y I_y \right) + Q \left( I_z^2 - \frac{1}{3} I(I+1) \right) - \beta g H \cdot I
$$

(2.1)

where S and I correspond to the ion’s electronic and nuclear spins, respectively.

Segment (2.1) of the Hamiltonian captures the electronic Zeeman effect, where $\beta$ is the Bohr magneton, $\mathbf{H}$ is the applied magnetic field vector, and $g$ is the spectroscopic splitting factor [11]. The
ZFS effect is accounted for by segment (2.2), where \( D \) is the crystalline splitting factor. Segments (2.3), (2.4), and (2.5) capture the effects of positive nuclear spin and are thus only included when \( I > 0 \). In this event, segment (2.3) captures the interactions between the electronic spin and nuclear spin, segment (2.4) adds the nuclear quadrupole term, \( Q \), and segment (2.5) represents the nuclear Zeeman effect, where \( \beta_n \) and \( g_n \) are the nuclear magneton and nuclear spectroscopic splitting factor, respectively.

The Hamiltonian parameters \( A, B, D, Q, g, \) and \( g_N \) have been extensively studied using paramagnetic resonance experiments for \( \text{Cr}^{3+} \) ions in chrome alums, though infrequently for CCA. A selection of observed values for these parameters for \( \text{Cr}^{3+} \) ions in CCA or similar crystals are given in Table 2.

| Parameter [Unit] | Value \( \times 10^4 \) | \( T \) [K] | Ref. |
|------------------|----------------|----------|-----|
| \( A \) [cm\(^{-1}\)] | 17.557 | 4.2 | [9] \( ^a \) |
| \( B \) [cm\(^{-1}\)] | 17.211 | 4.2 | [12] \( ^a \) |
| \( D \) [cm\(^{-1}\)] | -0.066±0.001 | 20 | [13] |
| \( Q \) [cm\(^{-1}\)] | 0.1547±0.0001 | 4.2 | [9] |
| \( g \) \( g \| \) | 1.9718±0.0050 | 4.2 | [9] |
| \( g \perp \) | 1.9722±0.0050 | 4.2 | [9] |
| \( g_N \) | -0.31114±0.00050 | 4.2 | [9] |

\(^a\)Values taken from [9, 12] are for \( \text{CsGa(SO}_4\text{)}_2 \) enriched with \( \text{Cr}^{3+} \).

3.2. Modelling method and calculations

The magnetic interaction Hamiltonian and experimentally determined parameters were used to develop a model for calculating the thermodynamic properties of CCA. Complete spin matrices for the \( \text{Cr}^{3+} \) ion for both parallel and perpendicular orientations of the applied field to the z-axis can be found in [10, 9]. Diagonalization of these Hamiltonian matrices gives the energy eigenvalues of the ion. The partition function can then be used to find the thermodynamic properties of the ions given these energy levels, and is defined as:

\[
Z = \sum_{\varepsilon} e^{-\beta \varepsilon}
\]  

(3)

where \( \beta \) is equal to \( (k_B T)^{-1} \), \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The expected energy, \( \langle E \rangle \), and heat capacity, \( C \), of the ion can then be determined using the following equations:

\[
\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}
\]  

(4)

\[
C = \frac{\partial \langle E \rangle}{\partial T}
\]  

(5)

Additionally, we calculated the predicted refrigeration capacity of the ion, which is defined as:

\[
T \frac{\partial S}{\partial B}
\]  

(6)

where \( B \) is the applied magnetic field and \( S \) is the entropy, calculated using:

\[
S = \frac{\partial (k_B T \ln Z)}{\partial T}
\]  

(7)
We had sets of data from two different CCA pills. This introduced an additional ions/g scaling parameter for each data set, representing the total number of Cr$^{3+}$ ions in the respective samples, and an effective field parameter, adjusting for possible off-centre axial suspension of the sample within the magnet bore and field edge effects. We performed a nonlinear least-squares analysis to find the best fit scaling values, and thoroughly investigated the effects of changing the various parameters listed in table 2.

3.3. Cr$^{3+}$ ion energy, magnetic moment, and heat capacity in CCA

To better understand the impact of the previously explained interactions, specifically the effects of ZFS, it is helpful to examine how they impact the energy levels of the Cr$^{3+}$ ion, and the resulting magnetic moment and heat capacity. An energy level diagram for the Cr$^{3+}$ ion in CCA with the magnetic field parallel to the z-axis is shown in the magnified portion in figure 1. The effect of trigonal compression of the water octahedron around the Cr$^{3+}$ ion can be seen, as the $\pm 3/2$ states are lower in energy than the $\pm 1/2$ states at zero field [10, 9]. At low enough temperatures, the energy difference between these sets of states at zero field and the points where they overlap at low fields have a significant impact on the energy and entropy of the ion. In terms of Hamiltonian parameters, this compression results in a negative D ZFS parameter [10, 9]. This distortion also increases the B hyperfine parameter relative to A for isotopes with nonzero nuclear spin [10, 9].

It is also informative to look at the effects of ZFS through comparison with the well-known Brillouin theoretical function, which gives the average magnetic moment per ion as a function of B/T [Tesla/Kelvin]. Without inclusion of the ZFS D term in the Hamiltonian for I=0 ions, agreement between magnetic moment predictions by the Hamiltonian and Brillouin function is quite good. The inclusion of this ZFS term results in the temperature dependent divergence shown in figure 2, where the magnetic field is assumed to be oriented along a crystal cubic axis.

Similarly, it is common to report heat and refrigeration capacity curves as a function of B/T. Figure 3 further highlights the consequences of ZFS as these predicted thermodynamic properties diverge from ideal paramagnetic behaviour at temperatures approaching zero Kelvin.

![Figure 2](image1.png)  ![Figure 3](image2.png)

**Figure 2.** Comparison between the average magnetic moment per Cr$^{3+}$ ion calculated by Hamiltonian and Brillouin function.

**Figure 3.** Heat and refrigeration capacity curves for Cr$^{3+}$ ion with and without ZFS.
4. Experimental design

4.1. CCA salt pill growth

Two CCA salt pills were grown from a solution onto a gold wire thermal bus mostly following the process described in Hagmann [14]. The compressed wire bundle was inserted into a close fit cavity in a high purity copper bus bar-steel cap assembly with normal metal braze powder. The assembly was then vacuum brazed and inspected by X-ray to verify complete fill of the braze material within the copper cavity and around the pressed gold wires. A completed salt pill thermal bus assembly is shown in figure 4. The thermal bus assembly was mounted in the crystal growth assembly shown in figure 5. A stochiometric mixture of Caesium Sulphate (Cs₂SO₄) and Chrome Alum (Cr₂(SO₄)₃·12H₂O) dissolved in a litre of 21% nitric acid was poured into the top of the growth setup. CCA crystal growth was initiated by cooling the thermal bus to a range of temperatures -10 °C to 3 °C using an array of thermoelectric coolers. Fresh solution was replaced roughly every week along with removal of stray crystal growth in flow channels on the side of the cylindrical mould region. Crystals were >90% complete after 6 weeks, removed from the mould and trimmed to slip fit into a stainless steel canister. CCA crystal growth was continuous across the thermal bus. Typical crystallite size was 5 mm, measured by picture scale. Adhesion between crystallites was substantially more robust than the ‘crumbly’ texture described by Hagmann. Measured mass, after trimming, of the crystals grown on to the thermal bus are given in table 3. A stainless steel canister was laser welded to the thermal bus assembly to hermetically seal the CCA against dehydration. Verification of the hermeticity of welding procedure was performed on an empty thermal bus canister assembly. The stainless steel canister was also thoroughly cleaned post fabrication.

![Figure 4](image1.png)  
**Figure 4** (right). Crystal growth station. Lucite container on top is filled with a saturated stochiometric solution in nitric acid. Two of six thermoelectric coolers (TEC) shown below lucite form. Waste heat from hot side of the TEC is removed using the aluminum heat exchanger and computer fan. The forced convection interacted exclusively with the heat exchanger at the bottom of the apparatus.

![Figure 5](image2.png)  
**Figure 5** (above). CCA grown on thermal bus (top) gold wires brazed into gold plated copper thermal bus (middle) with stainless steel cap and sleeve (bottom).

The completed salt pills were characterized using a vacuum insert dipped into a pumped liquid helium bath. The insert is equipped with a pumped ³He stage with a base temperature of ~ 300 mK. The heater and thermometer wires were heat sunk at the 300 mK stage and at higher stages to minimize parasitic heat leak into the salt pill. The salt pill was mechanically support and thermally isolated from the ³He stage using a ³He actuated gas gap heat switch made within a thin walled vespel tube. The heat switch actuation was managed with a room temperature gas handling system. The vacuum insert was located in the bore of a superconducting magnet immersed in the liquid helium. Base temperature of each CCA pill was below the quoted calibration range of the Ruthenium Oxide thermometer used on the sample. Using a standard calibration curve for this thermometer we estimate the base temperature...
achieved was ~ 20 mK. The CCA temperature increased from 20 - 50 mK in ~ 10 hours. Using this drift rate, the upper bound on the parasitic heat load from the 300 mK stage is of 20 nW.

Table 3. CCA pill assembly characteristics.

|       | Volume [cc] | Mass [g] | Cr\textsuperscript{3+} [mmol] | Gold wire [g] | Steel [g] | Copper [g] |
|-------|-------------|----------|-------------------------------|---------------|-----------|------------|
| CCA1  | 25          | 35.8     | 36                            | 13.9          | 11.4      | 28.4       |
| CCA2  | 25          | 30.5     | 30                            | 13.9          | 11.4      | 28.4       |

4.2. CCA heat and refrigeration capacity measurements
The heat capacity measurements were taken by applying heat pulses to the pill at regular intervals and measuring temperature change. The temperature measurement from an example pulse is shown in figure 6. To calculate the heat capacitance, a program in MATLAB was written to find linear fits to the first and second segments, and then extrapolated both segments to the centre of the heat pulse to find the corrected temperatures. These temperatures were used to find the ΔT associated with the pulse. We determined the change in energy from:

\[ Q = \frac{tV^2}{R} \tag{8} \]

where \( t \) is the duration of the heat pulse (20s), \( V \) is the voltage that is applied during the heat pulse, and \( R \) is the resistance of the heater (22906Ω). The applied voltages were adjusted to maintain a relatively constant ΔT value. The heat capacity is then calculated given:

\[ C = \frac{Q}{\Delta T} \tag{9} \]

The refrigeration capacity was also measured using the heat pulse technique, but instead of determining a temperature change we find the required decrease in applied field to return the system to the initial temperature following a heat pulse event. The change in field, along with the input energy found with equation (8), can be used to find the refrigeration capacity at a given temperature and field:

\[ \frac{\partial Q}{\partial B} \tag{10} \]

Figure 6. Method of determining heat capacity from heat pulse in paramagnetic salt. The settling time after the pulse is <1 minute and time span for a segment is 2 ~ 8 minutes.

Figure 7. CCA pill thermal resistance measurements fit to 1/\( T^3 \) compared with thermal resistance measurements of chrome potassium alum (CPA) to copper and ferric ammonium alum (FAA) to quartz.

4.3. Parasitic heat and CCA conductance measurements
Careful experimental design is crucial for minimizing losses and increasing measurement accuracy. We characterized such losses through conductance and thermal relaxation measurements, as well as estimates of parasitic heat as a function of the temperature of the measurement stage. As the temperature of the pill decreases, the parasitic heat from the precooling stage becomes more significant. Estimates
of this load at each experimental temperature point based on drifts in the baseline data were used to make corrections to the measured heat inputs and observed temperature changes. Following this adjustment, the maximum systematic error is estimated to be <0.4 mJ/K or <5.171e-25 J/ion-K. We measured thermal resistance between the thermal bus and the CCA for CCA1. Our conductance measurements fit to $1/T^3$ are shown in figure 7 which indicates thermal resistance limited by the CCA to gold boundary resistance. The absolute value of the thermal resistance is in family with other measurements in the literature as shown in figure 7 [14, 15]. Thus, the CCA is in good contact with the thermal bus. However, the literature values suggest that the thermal resistance could still be reduced by a factor of 3 if ideal surface contact is made between the CCA and gold [14].

5. Results
This investigation focused on quantifying the effects of different low temperature magnetic interactions, determining the heat capacity of CCA through experimental testing, and combining these efforts to improve the understanding and modelling of CCA properties. To understand which of the previously described effects has a material effect on the thermodynamic properties of the salt in the temperature range of interest, we explored the effects of changing select Hamiltonian values from table 2. As the nonzero isotopic abundance is only 9.5% for Cr, it is easiest to see the effects of the hyperfine interaction terms considering just the Cr$^{53}$ ion. Heat capacity curves for Cr$^{53}$ with the hyperfine A and B parameters at 100%, 200%, and 300% of their initial values are shown in the left plot in figure 9. Changing the ZFS factor, D, had the most noticeable effect on the overall heat capacity. Heat capacity curves with 85%, 100%, and 115% of the initial ZFS D value are shown on the right in figure 9. To highlight the sensitivity of the ZFS parameter, both plots are for a single Cr$^{53}$ ion and have the same ranges and scales.

For model fitting to experimental data, we excluded hyperfine interactions and assumed that the applied field was oriented along the cubic axis of the crystal. This orientation is at an angle $\theta$ relative to the trigonal axes, where $c = \cos^2 \theta = \frac{1}{3}$ for all four trivalent ions in the unit cell [16]. The energy levels for this orientation are taken from [16, 17]. As previously noted, the only independent fitting parameters are the ions/g scaling factor, which scales the model from a single ion to the total number of ions per gram in each pill, and effective field scaling factor, which scales the applied field for possible off-centred suspension and field edge effects. Because parasitic loads and measurement uncertainties increase at decreasing temperatures, we fit the independent parameters to the 300 mK measurements. Additionally, because addenda heat capacity potentially contributes to the heat capacity measurements, we fit the model to the refrigeration capacity data, which includes only magnetic contributions. Contour plots of the best fit values for this parameter space using a nonlinear least-squares analysis are shown in figure 9. The data points were weighted by both estimated measurement error and by distance from the centre of the 300 mK temperature peak, giving higher importance to the critical fit area.
The final values from this fit, as well as estimated parameter values, are given in table 4. The estimated field scale is calculated from averaging the actual applied field based on the magnet geometry over the crystal volume. The estimated ions/g is found using the molar mass and crystal structure of CCA. The measured specific refrigeration capacities, along with the capacities predicted by the model using the best fit parameters from table 4, are shown in figure 10 for the two CCA salt pills. Finally, to evaluate addenda heat capacity and entropy loss due to non-adiabatic effects we examined the experiment collection ranges in context of the entropy-temperature plane shown in figure 11. Here, the beginning and ending data collection points for each temperature are shown with the blue and red circles, representing CCA1 and CCA2 respectively. A magnetic refrigeration cycle is overlayed on this plot.

**Table 4.** Estimated and best fit parameter values for CCA1 and CCA2 refrigeration capacity data.

| Effective Field Scale | CCA1 | CCA2 |
|-----------------------|------|------|
| Estimated             | 0.87 | 0.87 |
| Applied               | 0.84 | 0.88 |

| Ions/g Scale          | CCA1     | CCA2     |
|-----------------------|----------|----------|
| Theoretical [ions/g]  | 1.02x10^{21} | 1.02x10^{21} |
| Fill Fraction [ions/g]| 0.77x10^{21} | 0.90x10^{21} |

**Figure 9.** Contour plots of best-fit statistic for scaling parameters from least-square fits to 300 mK refrigeration capacity data.

**Figure 10.** Model fit to CCA refrigeration capacity data with Cr^{3+} best fit parameters from table 4.
6. Discussion

The cooling capacity was measured for two CCA salt pills from 50 mK – 300 mK. The isolated paramagnetic spin model tells us that there should be a peak value of heat and refrigeration capacitance that is a function of the applied magnetic field, shifting to higher magnetic fields for higher temperatures. The measured cooling capacity shows significant reduction below this spin model for temperatures below 100 mK.

Modelling effort was undertaken to understand the physical origin of the reduction in cooling capacity of CCA below 100 mK. This model included terms in the magnetic interaction Hamiltonian that capture the ZFS and nuclear hyperfine splitting effects. To better understand the effects of these individual parameters, we performed a series of tests varying the starting parameters. Changing the A and B hyperfine parameters did not have a material impact on the total predicted heat capacity, as previously mentioned. In considering just Cr$^{53}$ (which has nonzero nuclear spin), we found that the greatest changes were seen at 50 mK, where increasing A and B to 200% and 300% of their initial values increased the peak predicted heat capacity by approximately 3% and 7%, respectively. We found that, out of the interactions considered, the ZFS factor had the greatest effect on the overall heat capacity and have shown this in figure 8. As with the hyperfine A and B parameters, changing the ZFS D parameter had the greatest effect on the lowest temperatures. An increase of 15% of the initial D value decreased the 50 mK peak heat capacity by approximately 10%. Though increasing the magnitude of the D value appears to better approximate the suppression of heat capacity at lower temperatures, this does not fit the general trend for the splitting parameter found in literature. D is temperature dependent, though is observed to decrease in magnitude approaching absolute zero [10]. Thus, an increase in the ZFS is an unlikely explanation for the experimental behaviour of the CCA salts at this temperature.
Though the model shows that the hyperfine splitting is not significant at temperatures >50 mK, the inclusion of the ZFS parameters results in qualitative agreement with data, as shown in figure 10. However, measured data at 50 mK still shows a significant reduction below model prediction.

From figure 11 we can see that in the low field, low temperature limit there is a transition to reduced capacity. The ideal ratio of $S=3/2$ to $S=1/2$ is $\ln(2)^{-1} \approx 1.44$; the model is pretty close to the isolated spin limits. Examination of figure 11 allows us to evaluate non-adiabatic losses as well. The magnetization at constant temperature is consistent with the modelled field curves. This agreement helps verify that the addenda heat capacity is small and cooled adiabatically with the salt. The thermal resistance measurement of the salt to the thermal bus and thermal relaxation times of the temperature measurement stage were also used to characterize addenda heat capacity and entropy loss. These checks find that the reduction in cooling capacity below 100 mK cannot be accounted for by excess addenda heat capacity or non-adiabatic effects.

7. Conclusion and future work
Inclusion of the ZFS term in the model developed in this work resulted in improved qualitative agreement with experimental data compared to the isolated paramagnetic spin model, though it does not fully capture the severe reduction in cooling capacity below 100 mK. The inclusion of hyperfine nuclear terms had a minimal effect on the overall fit, in part due to the relatively small abundances of isotopes with nonzero nuclear spins. However, even when modelling the heat capacity for single $\text{Cr}^{53}$ ion, the hyperfine contribution was small relative to other terms. ZFS was the most significant contributor to non-ideal paramagnet behaviour of the factors included in our analysis and modelling of CCA. ZFS is also significant in other alums such as CPA, which has slightly more complex behaviour due to numerous zero field splitting values [4, 13, 16]. CPA has an effective ZFS D parameter that is greater in magnitude than that of CCA, resulting in a greater reduction in predicted heat capacity at reduced temperature. Further exploration of ZFS parameters for different alums would be beneficial for improved material characterization and selection.

The discrepancies between observed and predicted magnetic behaviour could be due to a number of factors. There may be one or more significant low-temperature interactions that are unaccounted for, such as magnetic dipole interactions or exchange interactions. Magnetic dipole interactions become important at temperatures of about 200 mK in chrome alums and could be considered in future analysis [18]. Better agreement with experiment is found assuming that these interactions are large compared to exchange interactions, though researchers have experienced difficulties matching observed and predicted values even when focusing on magnetic dipole interactions indicating that this may not entirely explain the experimental data trends [19]. Alternatively, there may be systematic errors in the data collection methods or other losses that have not been accounted for. New measurements are planned to understand if the remaining discrepancy between the model and data is a systematic effect or a more fundamental feature of the salt. More specifically, we will repeat the measurements done on one of the CCA pills with a new setup and an additional thermometer. We also plan to include more measurements at temperatures between 50-150 mK, one measurement at 1 K, and possibly a measurement at 40 mK.

8. References
[1] Debye P 1926 Einige bemerkungen zur magnetisierung bei tiefer temperatur. *Annalen Der Physik*, 386 pp 1154–60
[2] Giauque W F 1927 A thermodynamic treatment of certain magnetic effects. A proposed method of producing temperatures considerably below 1° absolute *J. Am. Chem. Soc.* 49 pp 1864–70
[3] Black T 1961 Magnetic measurements on chrome-cesium alum below 1° K (Thesis) Rice University
[4] Bowers K D and Owen J 1955 Paramagnetic resonance II *Rep. Prog. Phys.* 18 pp 304–73
[5] Beevers C A and Lipson H 1935 The crystal structure of the alums *Proc. R. Soc. Lond. A Math. Phys. Sci.* 148 pp 664–80
[6] Cole D B, Wang X, Qin L, Planavsky N J, and Reinhard C T 2018 Chromium isotopes *Encycl. Earth Sci.* pp 256–62
[7] de Klerk D 1956 Adiabatic Demagnetization *Low Temperature Physics II / Kältephysik II* pp 38–
[8] Kittel C and Luttinger J M 1948 Crystalline stark splitting and microwave resonance absorption in paramagnetic salts *Phys. Rev.* 73 pp 162–72

[9] Danilov G 1971 ESR and ENDOR investigations of Cr3+ impurities in α, β and γ alums (Thesis) University of Ottawa

[10] Leclerc A 1977 Determination and analysis of the 53Cr3+ fine and hyperfine structure parameters in hydrated crystals from electron spin resonance studies (Thesis) University of Ottawa

[11] Kittel C 1949 On the gyromagnetic ratio and spectroscopic splitting factor of ferromagnetic substances *Phys. Rev.* 76 pp 743–8

[12] Danilov A G and Manoogian A 1972 Electron-nuclear double resonance of Cr3+53 in gallium alums II *Phys. Rev. B* 6 pp 4103–11

[13] Blearney B 1950 Paramagnetic resonance spectra of five chromic sulphate alums at low temperatures *Proc. R. Soc. Lond. A Math. Phys. Sci.* 204 pp 203–16

[14] Hagmann C, Benford D, and Richards P 1994 Paramagnetic salt pill design for magnetic refrigerators used in space applications *Cryo.* 34 pp 213–9

[15] Vilches O E and Wheatley J C 1966 Techniques for using liquid helium at very low temperatures *Rev Sci Instrum* 37 pp 819-31

[16] Hudson R P 1952 Properties of the Cr+++ ion in the paramagnetic alums at low temperatures *Phys. Rev.* 88 pp 570–2

[17] O’Brien M C M 1956 Antiferromagnetic state in the chrome alums *Phys. Rev.* 104 pp 1573–9

[18] Baker J M and B Bleaney 1955 *Proc. Int. Conf. Low Temp. Phys.*

[19] Beun J, Steenland M, Klerk D D, and Gorter C 1955 Magnetic researches on adiabatically demagnetized chromium methylamine alum *Phys. 21* pp 767–82

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