

Specific heat study on the $S=1$ one-dimensional antiferromagnet NDMAP at low temperatures and in high magnetic fields

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Abstract

NDMAP is a well-known low-dimensional antiferromagnet compound that has been the center of several studies in the last decade. Earlier this year, the similar $S=1$, 1-D antiferromagnet, NTENP, was found to have Tomonaga-Luttinger Liquid (TLL) behavior. This behavior was discovered through magnetic specific heat data taken in high magnetic fields. Some believe that TLL behavior also exists in NDMAP. To test this, specific heat data was taken for NDMAP over low-temperatures and in external magnetic fields up to 20 T. The results are currently inconclusive.

I. Introduction

This summer I investigated low-temperature properties of low-dimensional antiferromagnetic compounds under the mentoring of Dr. Yasumasa Takano. I examined two such compounds: NTENP [$\text{Ni}(\text{C}_9\text{D}_{24}\text{N}_4)(\text{NO}_2)\text{ClO}_4$] and NDMAP [$\text{Ni}(\text{C}_5\text{D}_{14}\text{N}_2)_2\text{N}_3(\text{PF}_6)$]. These compounds—with their quantum magnetic properties—serve as a basic tool for understanding more complex systems. The low-temperature properties of these compounds have been the topic of numerous studies over the past couple decades, and a more complete magnetic theory is the end goal of these efforts.

NDMAP and NTENP are interesting one-dimensional (1-D) chain systems—interesting because a low-dimensional structure dramatically enhances the quantum-mechanical behaviors. For magnetic materials to show quantum-mechanical, non-classical behaviors, the requirement is that the spin quantum number of the magnetic dipole moment be small: $\frac{1}{2}$ or 1. In our compounds, the nickel electronic spins, carrying $S=1$ and situated on the 1-D chain, interact antiferromagnetically (i.e., neighboring spins prefer to line up antiparallel). Also we term the systems as 1-D because the magnetic interactions occur primarily along the 1-D chain.

These particular systems are interesting because they have two competing magnetic tendencies when placed within a magnetic field: (1) the desire of the magnetic moments to interact antiferromagnetically within the chain and (2) the desire of the magnetic moments to align parallel to the external magnetic field. At a given external field and temperature, the magnetic moments will either arrange themselves in an ordered configuration or prefer to be disordered depending on which configuration minimizes energy and maximizes entropy. The minimizing of free energy—the compromise of the competing energy and entropy—is defined by Eq. (1):

$$F = U - ST, \quad (1)$$

where F is the free energy, U is the energy, S is the entropy, and T is the temperature. Whenever the compound changes from preferring one configuration to another, we observe a phase transition.

A phase transition, in general, can be conceptualized as a change in the ordering of a compound. We detect a magnetic phase transition by measuring the entropy of our system—a measure of the disorder of a system. But instead of measuring this quantity directly, we determine it indirectly by determining the heat capacity of our sample. From the principle quantity of heat capacity, we may extract the information about the entropy through the expression

$$C = T \frac{\partial S}{\partial T}, \quad (2)$$

where C is the heat capacity, S is the entropy, and T is the temperature (assuming that the magnetic field is held constant). For our particular antiferromagnetic compounds, we look for a peak in the heat capacities, which indicates the magnetic phase transition from an antiferromagnetic ordering to a paramagnetic ordering. From the knowledge of the magnetic phase transition, we gain valuable insight into the compound's magnetic interactions and behavior.

In my experiment, specifically, we are searching for a Tomonaga-Luttinger Liquid (TLL) behavior in the compound NDMAP to occur in the temperature region above the magnetic phase transition. Dr. Takano and his colleagues observed this behavior earlier this year with the related compound NTENP [1]. Because NDMAP is a similar compound with 1-D, S=1, antiferromagnetic properties, we believed that it would also exhibit this behavior.

A TLL is characterized by a gapless linear energy dispersion best recognized by a linear trend in magnetic heat capacity at temperatures just above the phase transition from an antiferromagnetically ordered state to a paramagnetically ordered state [1]. The TLL was first proposed by S. Tomonaga in 1950 [2]. This model describes interacting electrons in a 1-D conductor. Such a model exists because the more common Fermi liquid theory breaks down for a 1-D system. The Tomonaga model showed that under certain constraints, the second order interactions between electrons could be modeled as bosonic interactions even though electrons are fermions [2]. In 1963, J. M. Luttinger reformed the theory by showing that the constraints were unnecessary [3]. The possible TLL behavior of NDMAP has been discussed in at least two papers [1, 4]. In hopes of proving this behavior, we pursued accurate, multi-field, heat capacity measurements of fully deuterated NDMAP (d-NDMAP).

Instead of NDMAP, the sample we used was actually d-NDMAP. A compound grown with deuterium—a hydrogen with a neutron—rather than hydrogen reduces the heat capacity of the nuclear magnetic moments at low temperatures and at high magnetic fields. An ordinary hydrogen has only one unpaired nucleon, and this lone proton interacts with the field, affecting the heat capacity measurements. A deuterium atom, however, has two nucleons—a proton and a neutron—which are able to form a pair and balance their magnetic moments. Specifically, hydrogen has the nuclear spin $I=1/2$ while deuterium has the nuclear spin $I=1$. The net magnetic moment is smaller in the case of deuterium, so the deuterium has a smaller effect on the heat capacity measurements.

Again, an important property of this 1-D magnetic sample is that the spins may be treated quantum mechanically. The NDMAP sample approximately follows the Heisenberg model—meaning that the magnetic moments, in zero-field, don't prefer which direction or axis in 3-D

space that they align so long as they are aligned antiparallel to their neighbor. I say approximately because NDMAP does have a slight anisotropic—or directionally dependent—behavior along an axis. For this reason, we must align the external field parallel with the c-axis, the direction of the chains, when taking our heat capacity measurements.

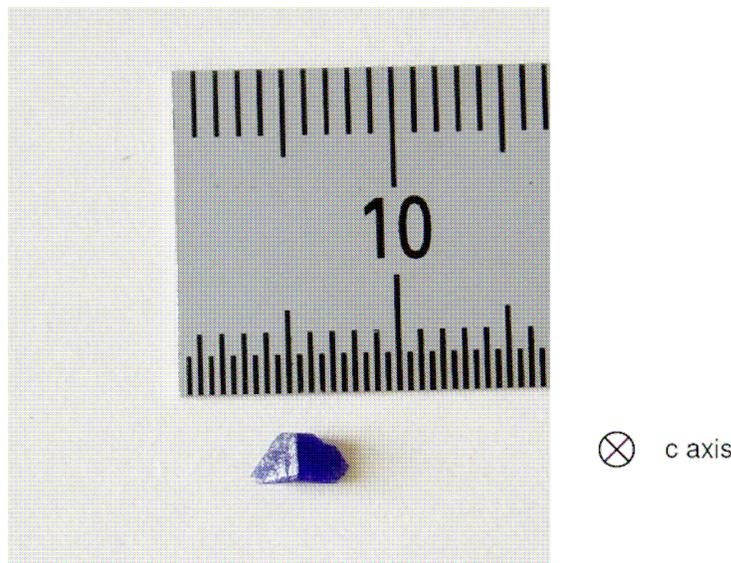


Fig. 1. Our single crystal sample of d-NDMAP. C-axis into the page. Photo by H. Tsujii.

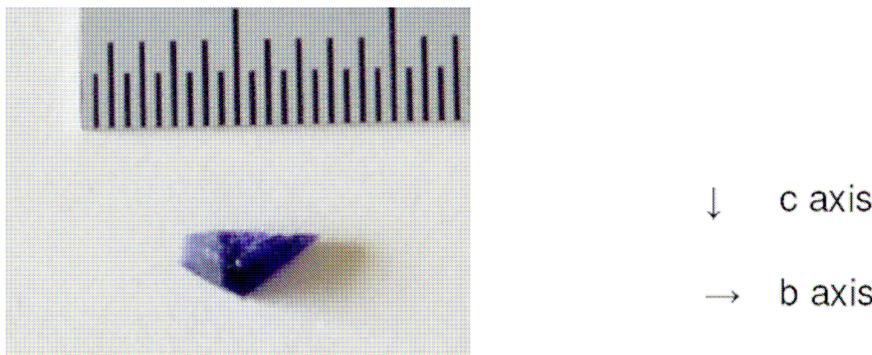


Fig. 2. d-NDMAP. Axes are labeled. Photo by H. Tsujii.

Figure 1 and 2 above depict the different axes of our d-NDMAP sample. Lining up the field along the direction of the chains, the c-axis, is necessary to detect TLL behavior through our heat capacity measurements.

II. Experiment

To measure the heat capacity, we used a standardized method, originally developed by Bachmann *et al.*[5]. To learn this method, the instruments, and data-collecting software, and to prepare for our true experiment in July, I took zero-field data of NTENP in Williamson Hall over the range of about 5 to 23 K. Later with our d-NDMAP sample, we performed our experiment in the 20 T superconducting magnet at the millikelvin lab at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida. Bachmann *et al.*'s apparatus is adapted for use in the NHMFL's top-loading dilution refrigerator in high magnetic fields [6]. The design of the apparatus—our calorimeter—is such that we can use a technique called relaxation [5]. The entire probe is approximately 1.5 meters long, so that it can be lowered into the mixing chamber of a dilution refrigerator, which cools to about 20 mK. At the very end of the probe, the vacuum-sealed can, which holds the calorimeter, is comprised of a relatively large silver block with a smaller silver ring welded to the bottom (See Figure 1). The sample is mounted on a sapphire platform in the center of the silver ring. We use silver in both cases because it has one of the smallest nuclear heat capacities—meaning the change in the heat capacity is relatively small compared to other metals when in the presence of an applied magnetic field. Both the block and the platform have heaters attached to a current source, and both have resistive thermometers to monitor the temperature of the calorimeter.

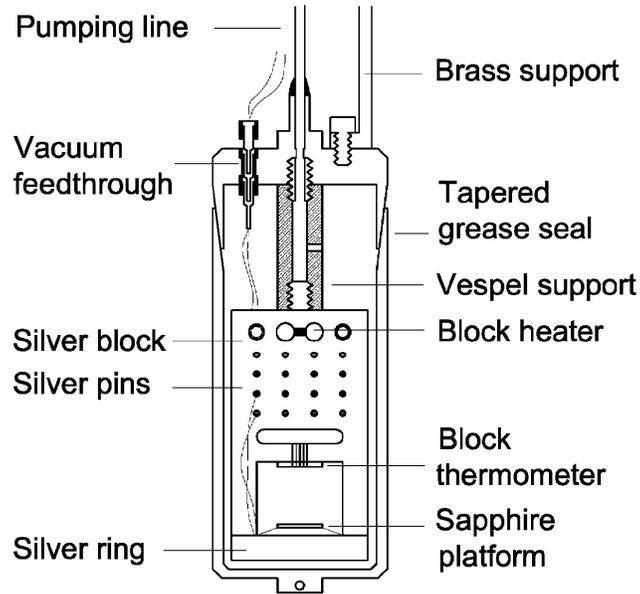


Fig. 3. Schematic cross section of the calorimeter cell [6].

The relaxation technique involves heating the block which consequently heats the platform through weak thermal links. Then we heat the platform to a temperature greater than the block, and because we have such a weak thermal link, the block should not be heated (given a proper amount of current to the platform heater, i.e. not too large). After heating the platform to the desired temperature, we then turn off the platform heater and let the temperature “relax” back down to the temperature of the block in an exponential decay. When modeling this relaxation method, we take advantage of the fact that under a small enough ΔT —under 5%—the relationship between the change in resistance of the platform thermometer ΔR is practically proportional to ΔT :

$$\Delta T \propto \Delta R . \quad (3)$$

We also acknowledge that through Eq. (4), ΔR is proportional to the off-balance voltage V of the Wheatstone bridge when the current I is held constant:

$$V = I\Delta R . \quad (4)$$

The design of the Wheatstone bridge allows us to use two known and equal resistors (R_1 and R_3) and a known variable resistor (R_2) to determine the value of an unknown fourth resistor (R_x)—our platform thermometer—by balancing the bridge voltage (attaining zero voltage). This setup is illustrated below as Figure 4.

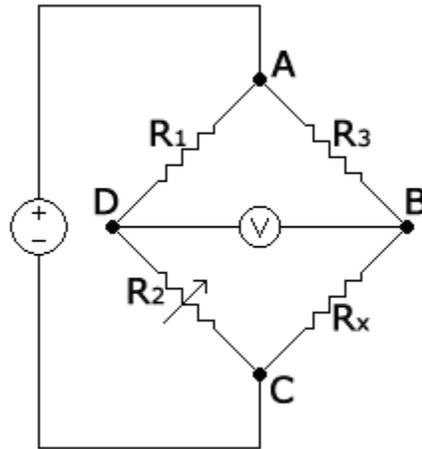


Fig. 4. Wheatstone Bridge. Base image courtesy of The Free Encyclopedia.

We obtain ΔR by balancing the bridge and recording R_x with the platform heater on and with the platform heater off. The off-balance voltage is the voltage we get by setting the variable resistor to the average of these two R_x values. We use the off-balance voltage to capture the average temperature during the relaxation (the voltage should zero at the midpoint of the data collection).

From these measurements, we are able to analyze the curves plotted for voltage against time and extract the time constant by Eq. (6).

$$V = V_0 e^{-t/\tau}. \quad (6)$$

Now equipped with our time constant, all we need is the thermal conductance of the weak link from the block to the platform to determine the heat capacity. A well-known definition of the thermal conductance is given by

$$\kappa = P/(T_1 - T_0), \quad (7)$$

where κ is the thermal conductance, P is the power, and $T_1 - T_0$ is the difference between the temperature of the platform and the block. Experiments have proven that the thermal conductance measured through this technique for low temperatures gives a slightly inaccurate heat capacity for milligram samples. Instead, Dr. Takano and his colleagues used a technique in which they measured the relaxation time of the platform plus a sample of high-purity copper and platinum—both of which are well-documented in heat capacity. By subtracting the known parts, Dr. Takano *et al.* calculated the thermal conductance by Eq. (8) and checked that the value is the same for both the copper and platinum measurements.

Having ascertained the time constant and the thermal conductance, we now calculate the heat capacity by

$$C = \kappa\tau. \quad (8)$$

Because this heat capacity is actually of the entire platform system, we subtract the heat capacities of the platform itself, and what remains is the heat capacity of our sample. Also we compute specific heat straightforwardly, by dividing the heat capacity by the mass of the sample and multiplying the result with the molecular weight.

III. Results

June

Our first trip to the NHMFL in June was primarily to calibrate the block thermometer of our new calorimeter. The current calorimeter design is not well-suited for magnetocaloric measurements, and we hoped our new calorimeter and calibration would enable us to take better

magnetocaloric data. The magnetocaloric effect is an intrinsic property of magnetic solids in which the solid responds to the application or removal of a magnetic field. Magnetic materials, by this effect, typically increase in temperature when in the presence of a magnetic field and decrease in temperature when the field is removed. The effect is maximized—reaches a peak—when the solid nears its magnetic ordering temperature. Part of our first trip also involved working to reduce the amount of noise received by our new design as is typical with low-temperature physics. Noise is the greatest obstacle of the low-temperature physicist. Noise causes heating of the system and also muddies the data, creating periodic or random variation in the data.

July

In July, we once again returned to the millikelvin lab at the NHMFL in Tallahassee, Florida. Using the same superconducting magnet as on our first run, we collected heat capacity data for most integer-numbered applied magnetic fields between 0 and 20 T. We made sure to collect as many measurements as necessary at each temperature to ensure a small error—below 1%. To cancel out noise and reduce error, we averaged all of the measurements for each data point; this reduced the error by approximately the square root of the number of measurements taken.

The data analysis had six basic steps: (1) read the printout of the measurements and remove any bad points (i.e. points corrupted by noise and points taken incorrectly), (2) average the measurements for each data point, (3) fit the averaged data points and extract the time constant, (4) construct a fit for the platform temperature calibration, (5) calculate the average

temperature of the platform, and (6) calculate the specific heat of the sample. The process involved a clever set of C programs, and the data analyzing program known as Origin™.

For my part, I analyzed the 0, 6, 8, 14, 16, 18, and 20 T fields. The results are displayed in Figure 5.

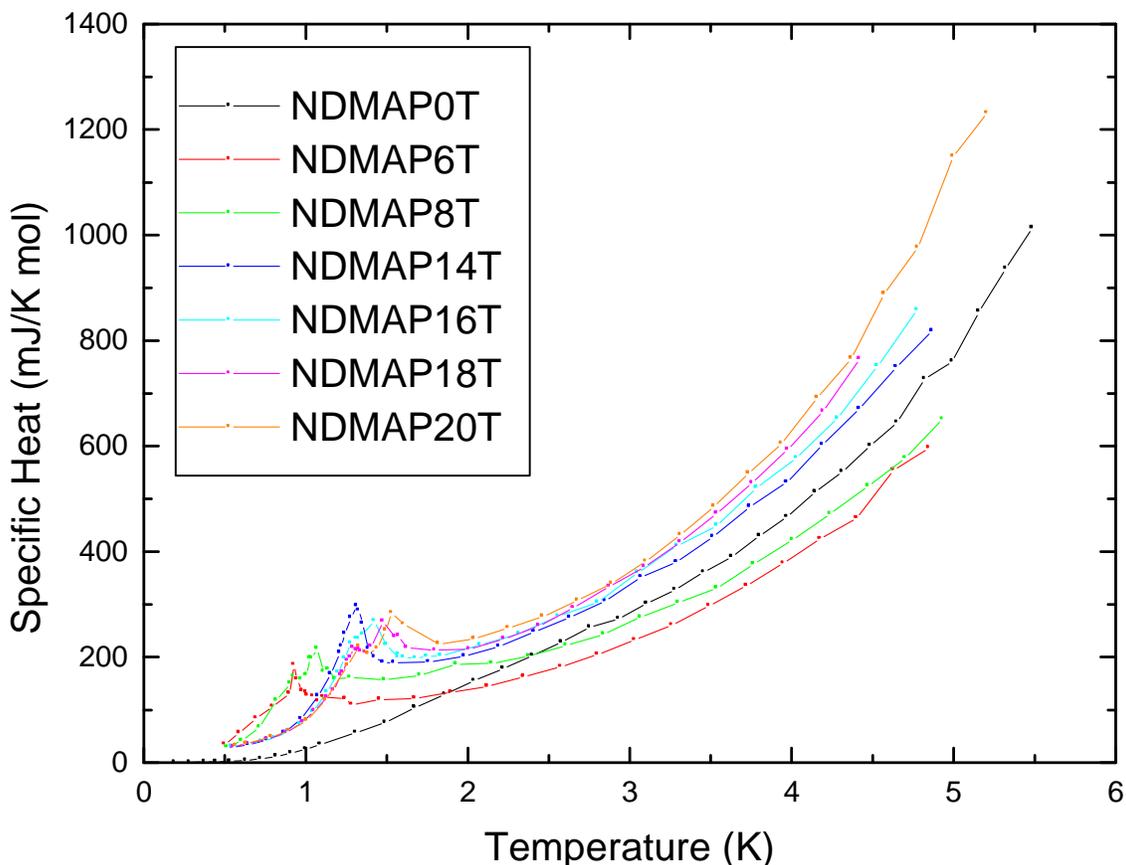


Fig. 5. Specific heat of deuterated NDMAP.

All the specific heat curves in applied fields exhibit the magnetic phase transition seen clearly as a peak in Figure 5. As the applied field increases, the highest peak of the curve shifts to a higher temperature. It is also apparent that the 18 and 20 T curves show two peaks; the first peak has a lower maximum while the second has a much higher maximum. When one looks closely at the lower fields, especially 16 and 8 T, a second peak seems to also arise, but it is a less drastic peak than at the higher fields.

Another part of the analysis involved subtracting the lattice contribution from the measured heat capacity. The lattice contribution is the uninteresting part of the heat capacity that is not dependent on the interaction between the magnetic moments or the external magnetic field. To subtract it, I performed a temperature-cubed fit for the zero-field data over the most important region—the region immediately following the phase transition. We noticed though, through this process, that our lattice contribution is inconsistent with the contribution measured by the grower of our crystal.

Nonetheless, I proceeded to subtract the lattice contribution, and the results are plotted in Figure 6. I performed this procedure for only the highest four fields because the 6 and 8 T fields clearly did not show signs of TLL behavior.

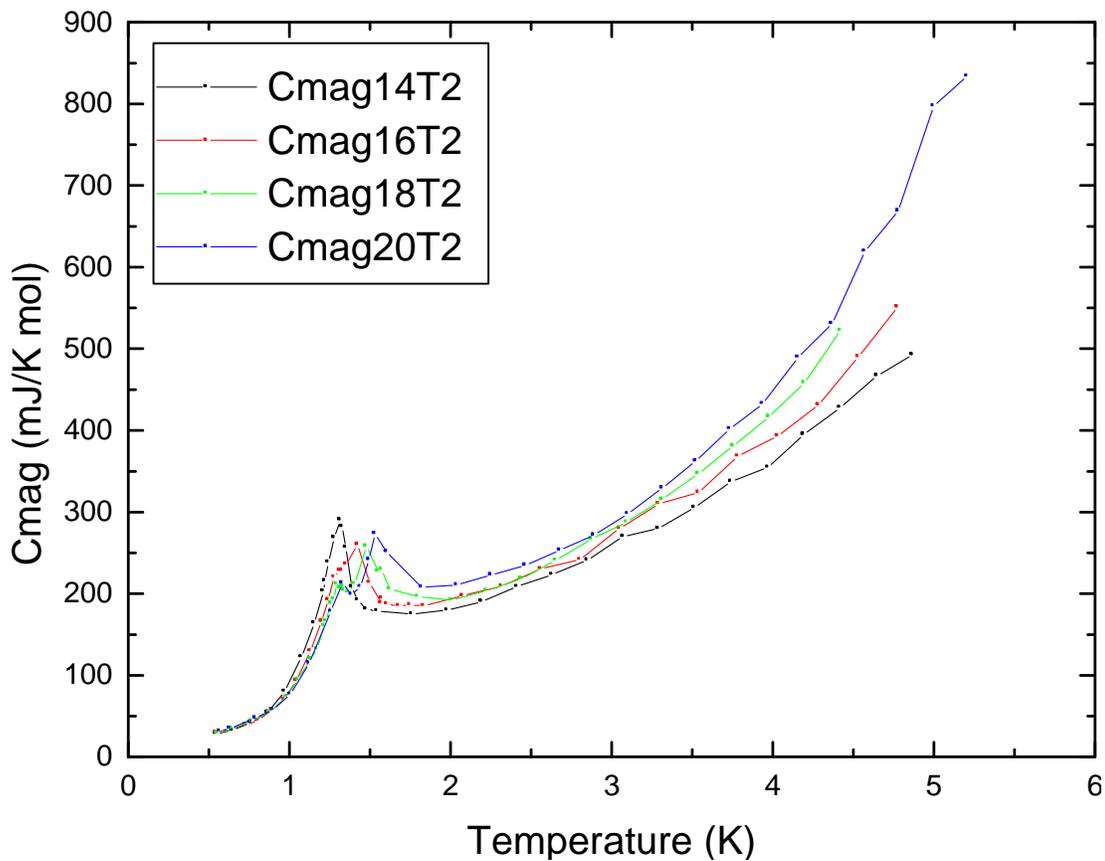


Fig. 6. Magnetic contributions to the specific heat.

Unfortunately, the magnetic contributions to the specific heat did not reveal the temperature-linear behavior that is characteristic of TLL (a line cannot be drawn in the specific heat data from the points in approximately the 2 to 3 K range through the origin).

IV. Conclusions

First of all, we must state that the data are not indicative of TLL behavior. That said, we still cannot rule out that d-NDMAP has this behavior due to the inconsistency between our determination of the lattice contribution, and the lattice contribution determined by the grower of our crystal. We believe that this inconsistency occurred because our sample cracked during the initial cool down to millikelvin temperatures. NDMAP has a known structural change at around 235 K which can cause a break in the structure of the crystal [7]. This break would cause the severed part of the crystal to have poor thermal conductance with the rest of the crystal (perhaps the severed part even fell off the platform), which would lower the measured heat capacities. The loss of mass would account for the inconsistency between the zero-field data taken by us and our grower. For this reason, we may seek to find a scaling factor for our specific heat data to find the true specific heat.

Another possibility which keeps me from entirely ruling out TLL behavior is that if the sample cracked, as we suspect, the severed piece may have changed its alignment with the field. In such a case, the specific heat data would be distorted, and no clear analysis could be made. The evidence for this case exists in the two peaks observed in the specific heat data. The NDMAP peak has been thoroughly investigated, and only one peak has ever been detected while aligned with an axis [4]. Therefore, the observation of a double peak lends credit to a severed

part of the sample changing its alignment with the field, creating a false peak in what should have been a strictly c-axis alignment.

Also in several earlier papers, the authors discussed that the existence of the alternating $\sim 15^\circ$ tilt of the main axes of the NiN_6 octahedra relative to the c-axis implies that no magnetic field direction strictly satisfies the symmetry for all the chains simultaneously [1, 8]. Or basically, because we cannot line up all of the magnetic moments along an axis with the field, evidence for a TLL in NDMAP will be difficult to attain. In any case, more data are needed to make a conclusive statement.

V. Acknowledgments

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References

- [1] M. Hagiwara, H. Tsujii, C. R. Rotundo, B. Andraka, Y. Takano, N. Tateiwa, T. C. Kobayashi, T. Suzuki, and S. Suga, *Phys. Rev. Lett.* **96**, 147203 (2006).
- [2] S. Tomonaga, *Prog. Theor. Phys.* **5**, 544 (1950).
- [3] J. M. Luttinger, *J. Math. Phys.* **4**, 1154 (1963).

- [4] H. Tsujii, Z. Honda, B. Andraka, K. Katsumata, and Y. Takano, *Phys. Rev. B* **71**, 014426 (2005).
- [5] R. Bachmann, F. J. DiSalvo, Jr., T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H.-U. Thomas, and R. B. Zubeck, *Rev. Sci. Instrum.* **43**, 205 (1973).
- [6] H. Tsujii, B. Andraka, E. C. Palm, T. P. Murphy, and Y. Takano, *Physica B* **329-333**, 1638 (2003).
- [7] M. Monfort, J. Ribas, X. Solans, and M. Font-Bardía, *Inorg. Chem.* **35**, 7633 (1996).
- [8] A. Zheludev, S. M. Shapiro, Z. Honda, K. Katsumata, B. Grenier, E. Ressouche, R.-P. Regnault, Y. Chen, P. Vorderwisch, H.-J. Mikeska, and A. K. Kolezhuk, *Phys. Rev. B* **69**, 054414 (2005).