

Quantum characterization of Ni₄ magnetic clusters using electron paramagnetic resonance

S. Maccagnano^{a*}, R. S. Edwards^b, E. Bolin^b, S. Hill^b, D. Hendrickson^c, E. Yang^c

^a Department of Physics, Montana State University-Bozeman, Bozeman, MT 59717

^b Department of Physics, University of Florida, Gainesville, FL 32611

^c Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093

Electron paramagnetic resonance is used to confirm the total molecular spin of Ni₄ molecular clusters and to determine if these clusters are single molecule magnets. Two Ni₄ clusters were examined, each with a different organic structure surrounding the molecule, to determine whether the magnitude of dipole-dipole interaction and quantum mechanical exchange could be quantified.

INTRODUCTION

Single-molecule magnets (SMMs) have quickly become an intensely studied material due to their intriguing quantum properties^{1,2}. The molecules consist of clusters of metal ions which couple together creating giant spins of up to $S = 10$ for some materials. Each molecule has a preferred axis for the magnetic moment of the molecule, called the easy axis, and each molecule is fixed in an organic lattice so that the preferred axes of all the molecules point parallel to each other. The lowest energy state for the molecule's magnetic moment either has spin projection $M_S = -S$ (up) or $M_S = +S$ (down), and there is a potential energy barrier preventing the flipping of spin from up to down and vice versa. At low temperatures SMMs exhibit many of the characteristics of ferromagnets; for example they exhibit magnetization hysteresis. However, unlike ferromagnets the SMMs display quantum tunneling of magnetization from up to down without input of energy³. These aspects are a trait of each individual molecule; so theoretically, each SMM would show a hysteresis loop and quantum tunneling. These quantum aspects of SMMs have aroused much interest not only for their novelty, but also because quantum magnetization tunneling could provide the superposition of states needed to produce quantum computer components.

* maccagnano@physics.montana.edu

The SMMs examined in this study consist of four nickel ions and four oxygen atoms forming the corners of a cube (Fig. 1). These samples were the first nickel SMMs synthesis attempted, so little was known about their quantum properties. Using hysteresis data, the spin of the Ni₄ molecule was estimated to be $S = 4$, but more definitive evidence was needed to determine conclusively the spin of the molecule and prove that this Ni₄ cluster was a SMM.

In SMMs, the metallic clusters are fixed in an organic lattice structure that affects the molecule in four important ways. First, it holds the molecules in such a way as to align the easy axes of magnetization for all molecules as mentioned above. Second, the lattice physically separates the molecules from each other so that there is very little dipolar magnetic interaction between molecules. Third, the lattice isolates the molecules from each other, thereby minimizing the quantum interaction between SMMs, called quantum exchange. Small variations in the lattice can cause large variations in the amount of quantum mechanical exchange possible between molecules. Fourth, though the overall lattice structure remains uniform, the local lattice structure at the site of the SMM itself can vary depending on the variety of ways the organic atoms can bond into the ligand[†], or how many isomers can be formed. Originally it was assumed that these isomers did not affect the quantum properties of the SMMs, but a recent study has suggested that isomers have a significant effect.⁴

The newly synthesized crystals that we studied were Ni₄ clusters with two types of ligand. The first crystal is [Ni(hmp)(EtOH)Cl]₄, or NiEtOH, whose ligand includes an ethyl group. The second crystal examined is [Ni(hmp)(MeOH)Cl]₄, or NiMeOH, whose ligand includes a methyl group. The ligand in NiMeOH is known to have a slightly shorter length than the ligand in NiEtOH, therefore causing the SMMs to be closer together in the lattice.

[†] Ligands are the organic strands that make up the lattice.

To understand the quantum properties of each SMM, we used a high frequency/field electron paramagnetic resonance (EPR) spectroscopic technique. Using the spectra obtained from each Ni₄ crystal, we can find the spin of the molecule, determine whether these molecules are SMMs, and observe the classical effects of dipole interactions between molecules and the stronger, more complicated effects from quantum exchange.

PROCEDURE

In SMMs, the unpaired-electron spins in the metallic clusters sum up to a total molecular spin of each SMM. For the sake of clarity, let us assume the total molecular spin is $\mathbf{S} = 4$. In each molecule, the angular momentum spin prefers to point along an axis. This preferred axis is called the easy axis. In the absence of an external magnetic field, each of the molecules preferentially aligns the magnetic moment either parallel or antiparallel to the easy axis such that the projection of the spin on the z-axis (parallel with the easy axis) is either $M_S = -4$ or $M_S = +4$. These preferred alignments are called the “spin-up” ($M_S = -4$) and the “spin-down” ($M_S = +4$), each having the same energy. In a classical system there would be an infinite number of spin orientations between the up and down states, but in quantum mechanics the number of spin orientations is limited, or quantized.

The spin orientations allowed for the molecular system we are considering would be quantized with each orientation differing by an integer (Fig. 2). Starting with spin up and looking at the projection of the spin orientation on the z-axis, the largest projection would be given by $M_S = -4$, and the next projection slightly smaller than the first would be $M_S = -3$. This would be followed by a smaller projection $M_S = -2$, and keep moving by integers until it reached a projection which has no magnitude on the z-axis at all, $M_S = 0$. As the spin orientation continues to “spin down”, the projections on the z-axis grow in

length until it reaches the largest projection again at $M_S = +4$. Therefore, there are $2S + 1$ spin projections, or for the case we are considering, nine spin states.

The energy associated with each orientation is also quantized, and is approximately

$$E = DM_S^2, \quad (1)$$

where D is a constant and M_S is the projection of the total spin $S = 4$ along the easy axis. Looking at the equation for energy (Equation 1), in the absence of a magnetic field the energy of the spin states is proportional to M_S^2 . This means that spin states with the same absolute value of projection ($M_S = \pm 2$, for example) have the same energy. In a SMM, the D value would be negative, causing the two spin states $M_S = -4$ and $M_S = +4$ to have the lowest energy. Each subsequent spin state increases in energy as the absolute value of M_S decreases, the highest energy state corresponding to $M_S = 0$. This describes two potential energy wells in spin space with minima at $M_S = +4$ and $M_S = -4$ and a potential barrier separating the two spin states (Fig. 3).

When an external magnetic field is aligned parallel to the easy axis, or z -axis, the spin states with angular momentum in opposite alignment with the field become preferred over those in alignment. This anti-alignment originates from the negative charge of the electron; the polarity, or magnetic moment, induced by the spinning charge points in the opposite direction to the spin angular momentum vector. In the presence of an external magnetic field, the equation describing the energy of the spin states gains another term,

$$E = DM_S^2 + g\mu_B BM_S, \quad (2)$$

where g is the proportionality constant called the Landé g -factor, μ_B is the value of the Bohr magneton, and B is the magnitude of external magnetic field. The Landé g -factor is a tensor, but the only component discussed in this paper is that along the z -axis, or g_z . Now, as we move away from zero magnetic field, the energy levels for the $M_S = \pm 4$ spin states begin to split. The $M_S = -4$ becomes a favored state as its energy decreases while the $M_S = +4$ state energy increases. This splitting in the presence of a magnetic field is called the Zeeman effect. An energy diagram showing the Zeeman splittings for the NiEtOH crystal is shown in Fig. 4.

Whether in zero-field or in the presence of a magnetic field, the energy of these spin states can be measured using EPR. EPR detects the energy required to make a transition between spin states. While the magnetic field is oriented along the easy axis, the only allowed transitions are between spin states that differ in M_S by ± 1 . The equation for the energy of these transitions is $\Delta E = \pm C_{ZF} \pm g\mu_B B$, where $C_{ZF} = (2M_S - 1)D$ is the energy of the transitions at zero field.[‡]

In this experiment, we placed the samples of Ni4 in a copper cavity that is inductively coupled to incoming and outgoing wave-guides. One wave-guide brings in a fixed-frequency/fixed-energy microwave, the microwave then interacts with the Ni4 crystal, and the second wave-guide transmits the microwave back to the detector. The detector and microwave source is a Millimetre-wave Vector Network Analyzer (MVNA)⁵. The highly-sensitive MVNA is able to detect small differences between the intensity of the initial microwave sent into the cavity and the intensity of the microwaves after they leave the cavity. The crystal and cavity are placed in the middle of a superconducting magnet. The magnet is kept superconducting by surrounding it with liquid helium, which also provides the capability of cooling the sample down to $\sim 1.8\text{K}$ for the experiments.

[‡] This equation is found by taking the difference between the energy of M_S and the energy of $M_S + 1$.

Heaters also allow us to heat the sample to temperatures above the boiling point of helium. Thus, the temperature of the sample can be set and held for each run. During a run, the magnet is swept from 0-6T, and microwaves are sent through the wave guides to the cavity and the sample. When the microwave photon energy exactly matches the transition energy between two adjacent spin states in the sample, the crystal absorbs the microwave energy and produces an absorption resonance (Fig. 5).

To begin analysis of an SMM, the location of the easy axis is needed. Though the crystal has a certain symmetry, the magnetic easy axis is not necessarily along any principal crystal axis. Therefore, we cannot visually determine which orientation of the crystal will be aligned with the easy axis. To find the easy axis, we exposed the crystal to a certain frequency of microwave radiation while changing the orientation of the crystal. The magnetic field was swept from 0 to 6 T and back down for each angle. Fig. 6 shows one transition's movement in magnetic field for seven angles. Because the EPR transitions occur at lowest field when the field is aligned along the easy axis, we were able to locate the easy axis by following the angle dependence of one transition peak that appeared in all of the field sweeps, such as the transition shown in Fig. 6, and graphing the location of this transition as a function of field and angle. We fit this graph with a $\cos^n\theta$ curve and were able to find the minima from the fitting function.

The easiest way to describe why transitions would occur at lowest field while the field was aligned with the easy axis can be seen by writing the transition energy equation again,

$$\Delta E = \pm C_{ZF} \pm g\mu_B B \cos\theta, \quad (3)$$

this time considering θ , the angle between the magnetic field and the z-axis. When the angle between B and z is large, $\cos\theta$ is small and B must be large to maintain the

transition energy between the states. As B and z align, the magnitude of B reaches its minimum value.

After the easy axis of the SMM was identified, this angle was examined carefully by taking many spectra at one temperature and angle and many different frequencies (frequency-dependent spectra) and also by taking many spectra at one frequency and angle and many different temperatures (temperature-dependent spectra). The frequency-dependent spectra can provide us with the transition energies for each set of transitions; $M_S = -4$ to $M_S = -3$, $M_S = -3$ to $M_S = -2$, etc. The locations of each transition in magnetic field are graphed for each frequency, and the data points are fit with the theoretical transition energy equation to find the total molecular spin S and the parameters D and g. This fitting is a difficult process that includes some fourth-order terms not shown in Equation 3 that often come into play in these materials, so a fitting program was used. This fitting can also be used to understand transitions that occur when the magnetic field is applied in any direction. These off-axis transitions are harder to understand since spin states become mixed as the magnetic field pulls the molecule's spin away from its preferred easy axis.

The temperature-dependent spectra give additional information about the SMM. When the temperature of the sample is very low, there is little thermal energy available to allow transitions from a high-energy spin state to a higher-energy one. Therefore, during low-temperature sweeps ($\sim 1.8\text{K}$), most of the resonance intensity is concentrated in one transition—the lowest energy ground state transition from $M_S = -4$ to $M_S = -3$. In this way it can be determined with quick observation of the spectra whether or not this Ni₄ cluster is a SMM. If a ground-state transition is observed, the Ni₄ clusters are SMMs, if not they are simple crystals. Also, the temperature-dependent spectra can reveal important things about population of states, the ground state, and which transitions are related to the ground state and which are not.

The temperature-dependent spectra can also give some indication of how the SMMs in the sample are interacting with one another. These interactions can include dipole-dipole and quantum exchange. Dipole interactions would cause a shifting of each resonance in the magnetic field at different temperatures through a Boltzmann factor that affects the magnetization of the sample (Fig. 7)⁶. This magnetization added to the applied magnetic field, H , is the true location in magnetic field, B , for each transition. This can be seen by the equation for the magnetic field felt by each molecule, $B = \mu_0(H + M)$, where μ_0 is the permeability of free space, H is the applied magnetic field, and M is the magnetization of the sample. Therefore, since the graph of transitions as a function of applied field that is seen in these studies does not take into account magnetization of the sample in addition to applied field, we will see a shift in the locations of transition as the magnetization shifts in magnitude with temperature.

RESULTS

NiEtOH

To determine if NiEtOH was an SMM, first the easy axis needed to be found. The process described above in Procedures was used, and the easy axis of the crystal was found to be 21° from an arbitrary zero point as marked on our instrument (Fig. 6). Once this easy axis was determined, many more EPR spectra were obtained.

The spectra for the NiEtOH crystal are not straightforward, with many multi-peaked resonances and shoulders, but in the easy-axis temperature-dependence spectra a relationship between these peaks is seen (Fig. 8). The two resonances at lowest field both grow in intensity as the temperature decreases, while all other resonances decrease. Since the only transition that increases in intensity as temperature drops is the ground-state transition, both of these resonances must correspond to the -4

to -3 transition. As transitions tend to be evenly spaced from each other, two sets of resonances are identified, labeled “majority peaks” and “X peaks” (Fig. 9). As the inset to Fig. 9 shows, the majority resonances are not sharp and well defined, but wide and made up of many individual resonances. For the subsequent analysis, the field corresponding to each majority peak was taken to be the center of the wide, multi-peaked resonance.

In the temperature-dependent spectra, the transitions show a slight but smooth widening of the peak and shifting of the peak in magnetic field. The shifting is easiest to see in the high fields, around 5-6 tesla. This shifting is similar to the trend of shifting seen in other SMMs, notably the Fe8 crystal⁷.

The two sets of resonances, majority and X, were analyzed separately, and the locations in magnetic field of the resonances were picked and graphed for many frequencies (Figs 10, 11). The X resonances were fit with the energy transition equation **(3)**, and NiEtOH was found to have a total molecular spin of $S = 4$, $D = -20.2$ GHz, $g_z = 2.24$, and $\theta = 0$ corresponding to the magnetic field being parallel to the easy axis. The majority resonances were fit with $D = -18.3$ GHz and $g_z = 2.20$.

NiMeOH

The easy axis for the NiMeOH was found in the same way as it was found for NiEtOH. The temperature-dependent spectra again show two of the resonances becoming most intense as the temperature decreases (Fig. 12). These two resonances were considered the ground state transitions and labeled the A resonances and B resonances (Fig. 13). These two sets of resonances are similar to those found in NiEtOH, except the paired NiMeOH resonances are further apart in magnetic field than those of NiEtOH.

In the temperature-dependent spectra, the transitions are seen to widen and shift in magnetic field in an irregular fashion. This is especially evident in the high-field transitions around 4-6 tesla.

The two sets of resonances, A and B, were analyzed separately, and were fit with the energy transition equation (Equation 3). Both sets of resonances confirmed that NiMeOH has a total molecular spin of $\mathbf{S} = 4$. The spectra with the A and B resonances were taken with the magnetic field parallel to the easy axis, so $\theta = 0$ in equation (Equation 3). The A-resonances were found to fit with $D = -1.5$ GHz and $g_z = 2.24$. The B-resonances were found to fit with $D = -15$ GHz and $g_z = 2.24$. (Fig. 14)

DISCUSSION

NiEtOH

Though the existence of an easy axis for these crystals does not prove that the samples are SMMs, it is along this axis that we should find only one ground state transition at lowest temperatures. The fact that we observed the transitions at higher field disappearing and the intensity of the two lowest field transitions increasing as temperatures decreased shows confidently that these Ni⁴ samples are SMMs. The mystery, however, is why there are two resonances exhibiting ground state behavior instead of one. In the case of the NiEtOH, we believe that each ground state transition represents a different isomer, or variety, of SMM in the crystal. In fact, when the majority peak is carefully examined, it is seen to consist of around four or five separate peaks, each one of which may represent a different isomer.

The fact that these crystals are indeed SMMs is confirmed when the frequency-dependent data are fit and the constant D is found to be negative.

The gradual and regular shift of the location of transitions in the magnetic field in the temperature-dependent spectra indicates the presence of some kind of exchange⁸.

More analysis is needed to determine whether this shifting is due to dipole-dipole interaction or quantum exchange.

NiMeOH

Not surprisingly, these crystals are also found to be SMMs, as shown both by the existence of ground state resonances and by the frequency-dependent data producing a negative-D-value fit. These crystals, like the NiEtOH, also have two apparent ground state transitions, but these resonances do not behave in the same way in the temperature-dependent spectra.

Due to the two, large ground-state transitions, it is likely that there are at least two isomers present in the NiMeOH crystals, but all of the unusual peaks cannot be explained by isomerism. Also, the high-field transitions shift with temperature in a more irregular manner than can be explained using only dipole-dipole interactions. These unexplained peaks and shifting are likely due to quantum exchange—stronger evidence for quantum exchange than was seen with the NiEtOH samples. This makes sense when one considers that quantum exchange occurs over short distances, and therefore the further apart the molecules are the less quantum exchange one would expect. Since the ligands in NiMeOH are shorter than the ligands in NiEtOH, the SMMs in the NiMeOH are closer together than those in the NiEtOH.

CONCLUSION

The Ni⁴ crystals examined in this study were found to be single molecule magnets. Further, the parameters for the energy equation were found for each different molecule studied. Indications that dipole-dipole interactions were present occurred in the samples, but what appear to be quantum exchange interactions in the NiMeOH mask the dipole interactions.

Further analysis will be undertaken on these samples. For example, the shift in magnetic field that the transitions undergo in the temperature-dependent spectra can be studied to determine if both X peaks and majority peaks show the same behavior. This way the contribution from the dipole-dipole interaction can be determined, opening the way for understanding the remaining behaviors that may belong to quantum exchange.

Also, new Ni₄ crystals are being synthesized with even longer ligands separating the molecules. These longer ligands should lead to less quantum exchange, and may be compared with the results from this study to understand the role of quantum exchange in these systems. The EPR spectra from these can be compared with the NiEtOH and NiMeOH and help isolate those behaviors that are due to dipole-dipole interactions and those due to quantum exchange.

ACKNOWLEDGEMENTS

The National Science Foundation and University of Florida REU summer program supported this work.

¹ J. Miller and A. Epstein, MRS Bull. November 2000, 21.

² S. Hill, J. A. A. J. Perenboom, N. S. Dalal, T. Hathaway, T. Stalcup, and J. S. Brooks, Phys. Rev. Lett. **80**, 2543 (1998).

³ K. M. Mertes, Yoko Suzuki, M. P. Sarachik, Y. Paltiel, H. Shtrikman, E. Zeldov, E. M. Rumberger, D. N. Hendrickson, and G. Christou, Phys. Rev. Lett. **87**, 227205 (2001).

⁴ S. Hill, S. Maccagnano, Kyungwha Park, R. M. Achey, J. M. North, and N. S. Dalal, Phys. Rev. B **65**, 224410 (2002).

⁵ Monty Mola and Stephen Hill, Rev. Sci. Instrum. **71** (1), 186-198 (2000).

⁶ B. I. Bleaney and B. Bleaney, Electricity and Magnetism, 3rd ed. (Oxford University Press, 1976), p. 482.

⁷ S. Maccagnano, R. Achey, E. Negusse, A. Lussier, M. M. Mola, S. Hill, and N. S. Dalal, Polyhedron **20**, 1441 (2001).

⁸ Kyungwha Park, M. A. Novotny, N. S. Dalal, S. Hill, and P. A. Rikvold, arXiv/cond-mat 0204481, 2002 (unpublished).

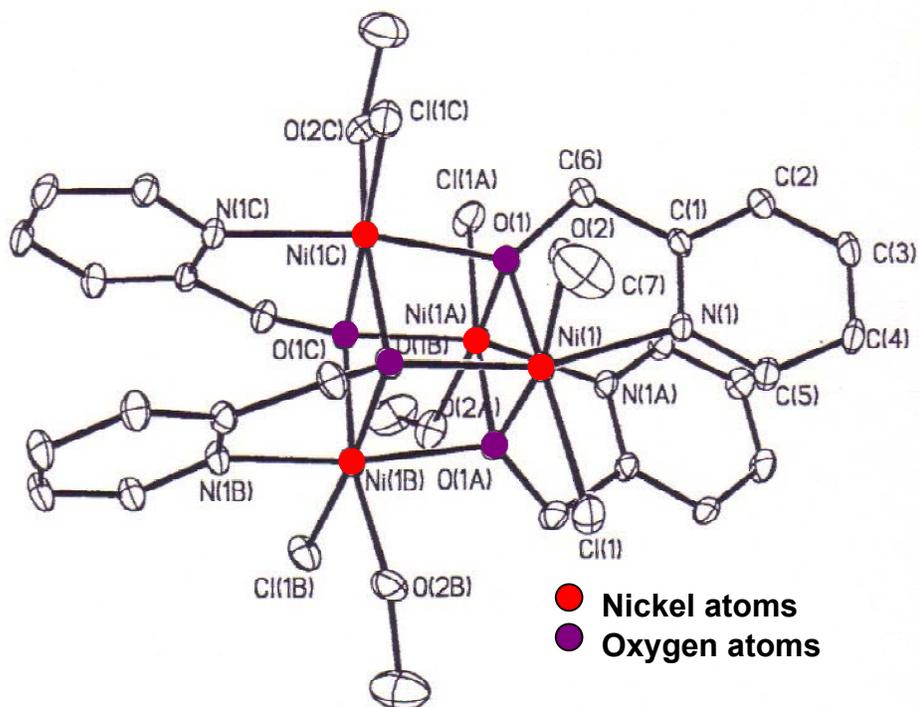


Fig. 1 Diagram of the Ni₄ molecule showing the arrangement of the nickel ions in relation to the oxygen atoms and the surrounding organic ligands. Metallic clusters create the magnetic properties of the molecule and the organic ligands hold the clusters apart from one another.

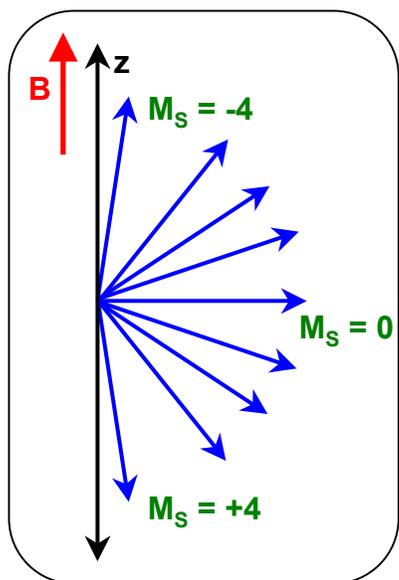


Fig. 2 Spin level diagram showing the allowed spin orientations for the Ni₄ clusters. When analyzing the easy axis, the external magnetic field is parallel to the z-axis.

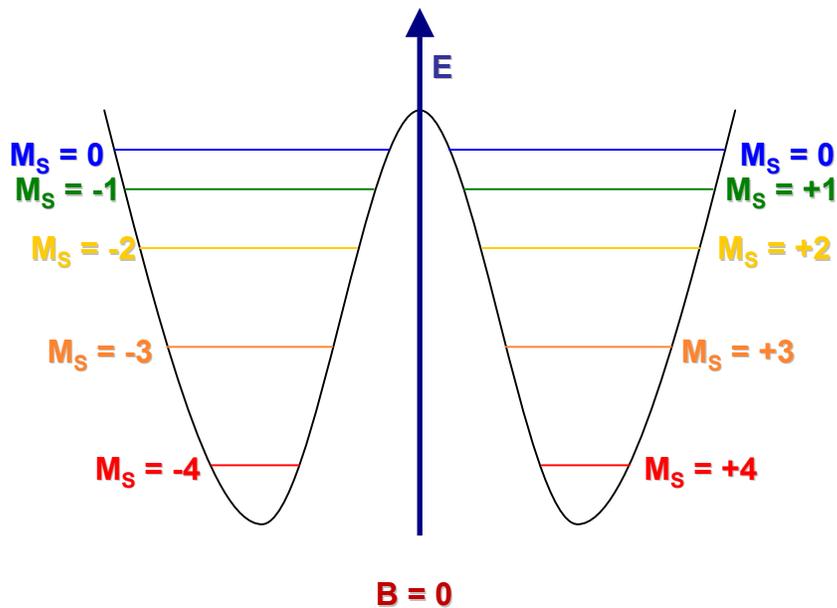


Fig. 3 The energy of the $S = 4$ spin states can be thought of as two potential energy wells in spin space. The lowest energy states are found in the bottom of the wells as $M_S = \pm 4$, and to get from $M_S = -4$ to $M_S = +4$ energy must be added to overcome the energy barrier between them. In zero magnetic field, the energy is the same for spin states whose absolute value of M_S are equal.

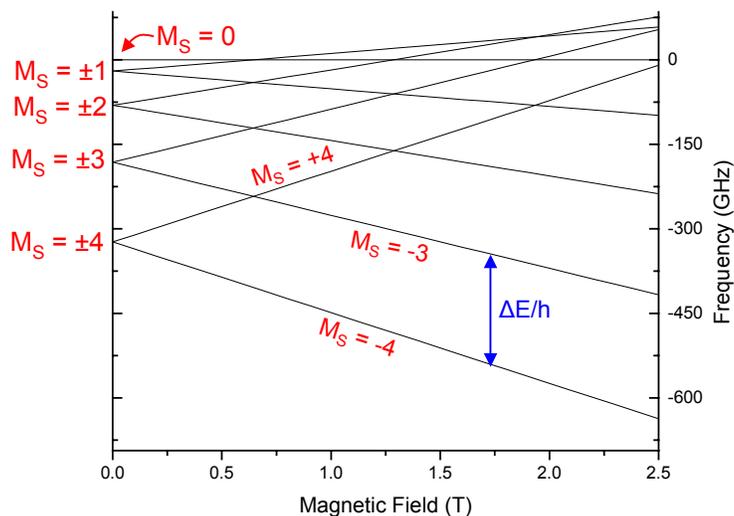


Fig. 4 Energy diagram for the Ni4EtOH showing how the energies of spin states split as field is applied. The amount of energy between adjacent spin states whose M_S differ by ± 1 is shown by the arrow $\Delta E/h$. If this amount of energy was available to the molecule at this magnetic field, a transition would be excited from $M_S = -4$ to $M_S = -3$.

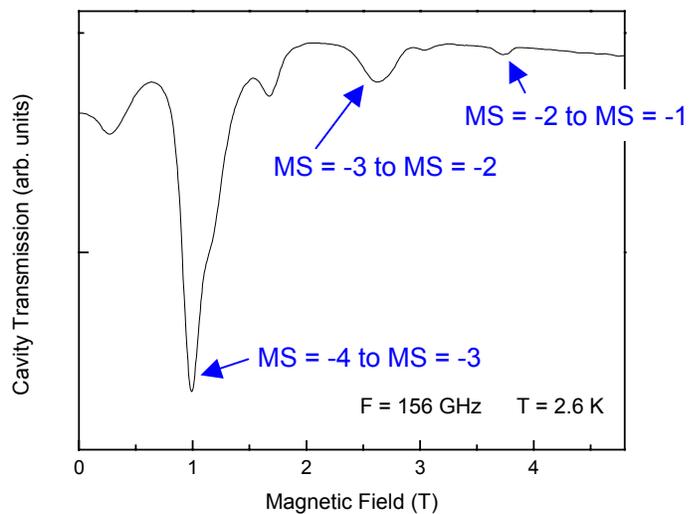


Fig. 5 Spectra showing spin transitions in Ni4 crystal. Blue arrows point to locations of transitions.

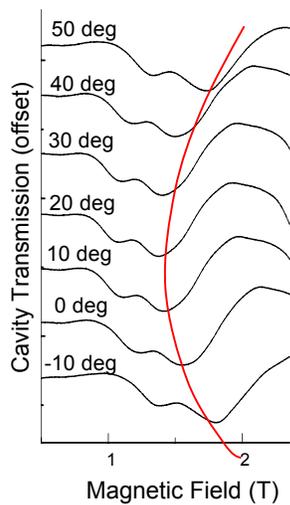


Fig. 6 Spectra showing the angle dependence of the transitions in magnetic field. This spectra for NiEtOH gives an angle for the easy axis at 21 degrees from an arbitrary zero of our instrument. The angle-dependent spectra were taken with a frequency of 133 GHz.

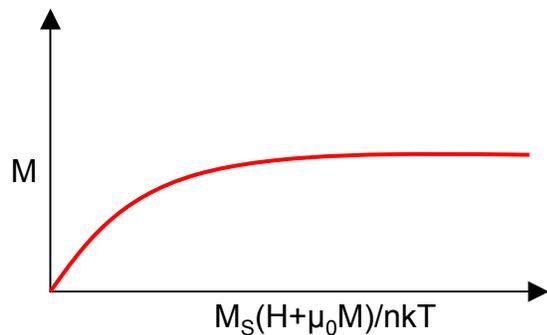


Fig. 7 Curve of magnetization of sample as a function of $1/T$. As temperature changes, the magnetization of the sample varies in a nonlinear fashion.

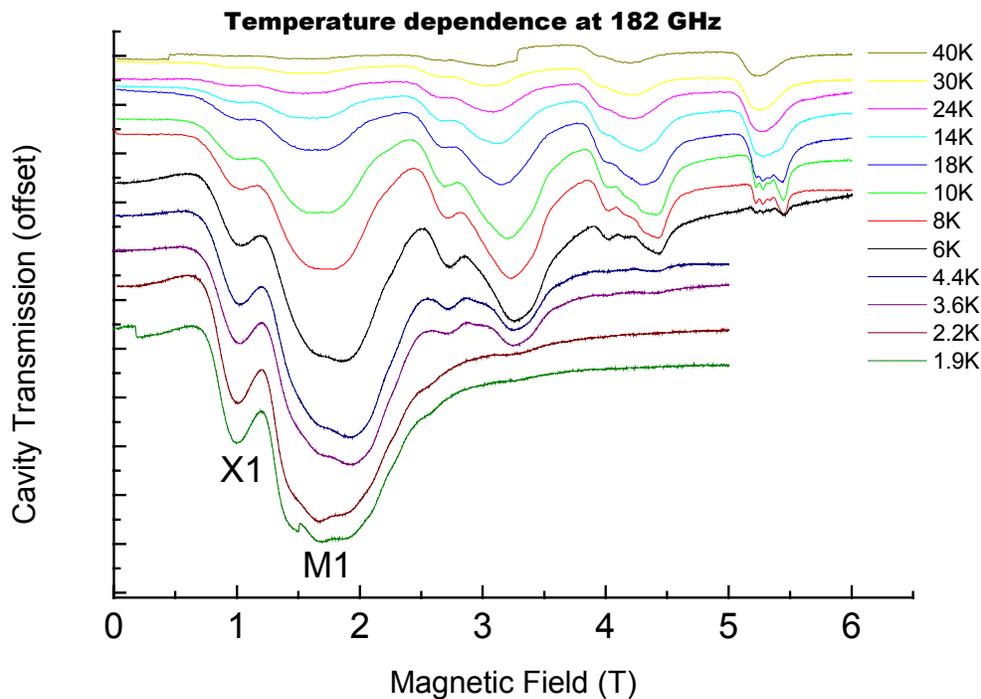


Fig. 8 Temperature dependence spectra of NiEtOH. Two resonances dominate at low temperatures, labeled X1 and M1 on the graph. These spectra were taken with a frequency of 182 GHz.

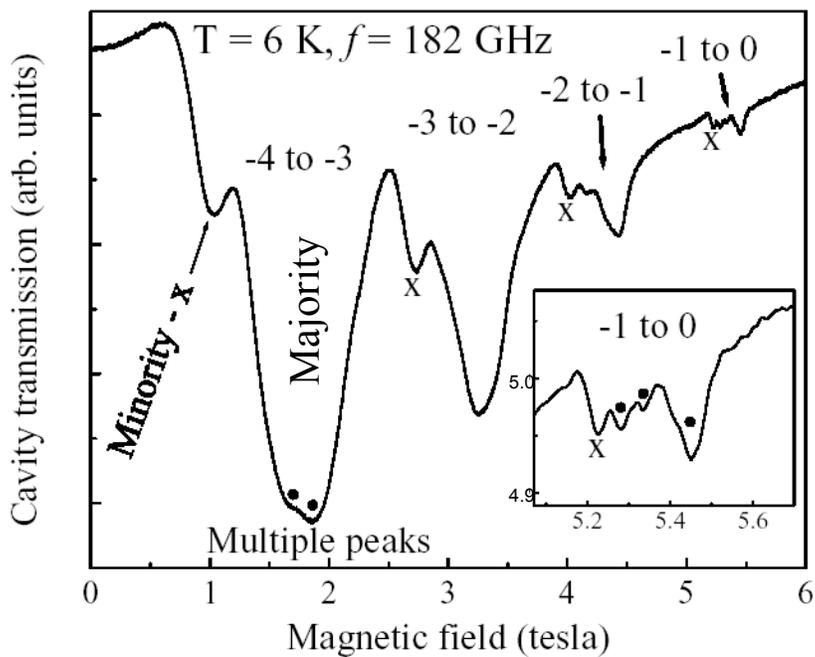


Fig.9 NiEtOH spectrum, made up of majority peaks (labeled by the initial and final spin projections) and minority (labeled X) peaks. Inset—Each majority peak is made up of multiple resonances.

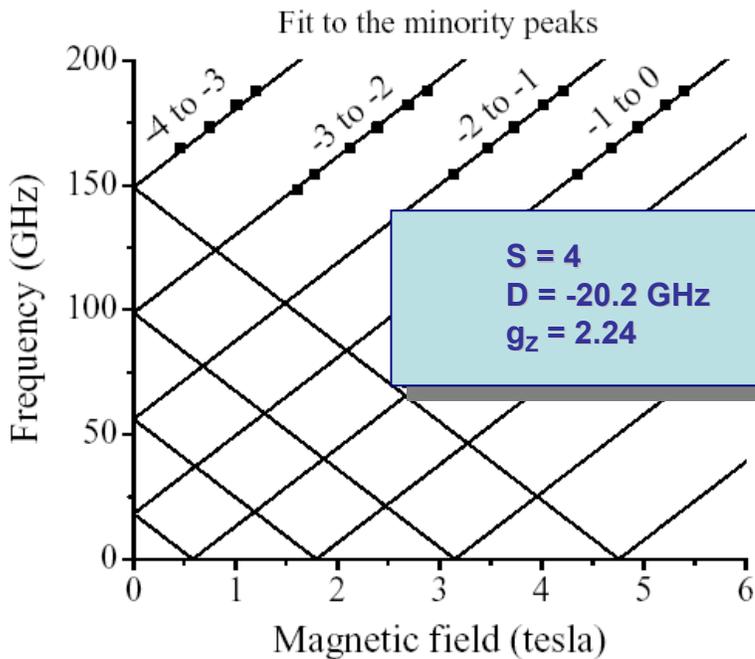


Fig. 10 Minority (or X) resonances graphed as a function of the frequency and magnetic field and fitted to find the total molecular spin, D, and g_z for NiEtOH.

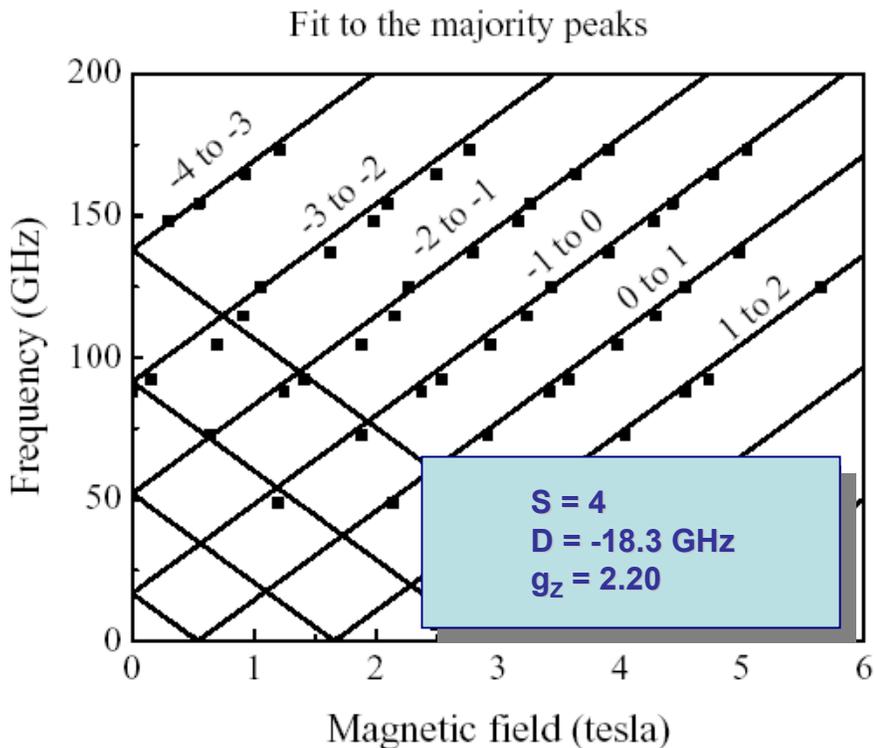


Fig. 11 Majority resonances graphed as a function of frequency and magnetic field and fitted to find the total molecular spin, D, and g_z for NiEtOH.

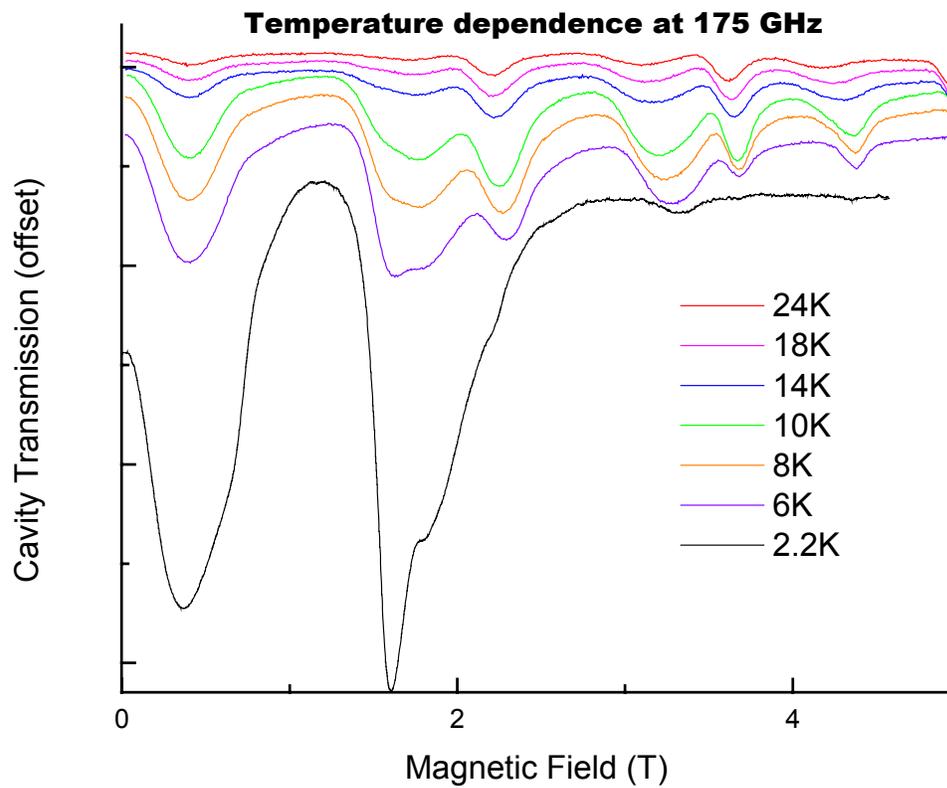


Fig. 12 Temperature dependence of the spin transitions for the easy axis of NiMeOH.

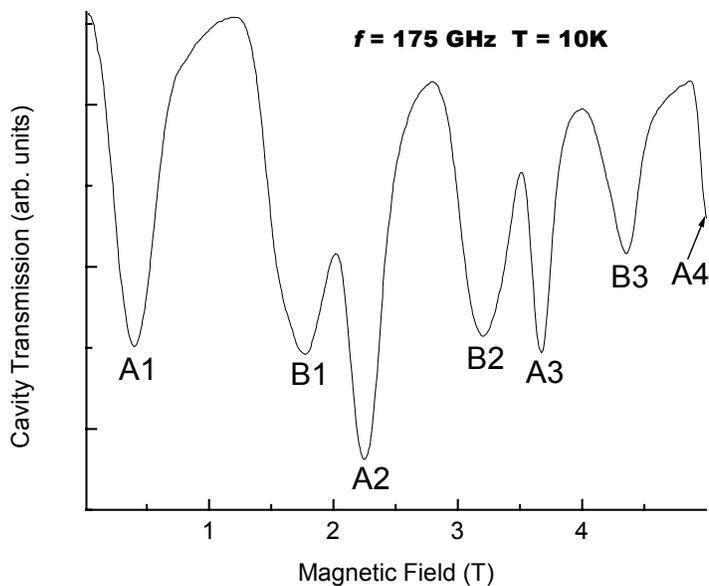


Fig. 13 Two sets of resonances are evident from the NiMeOH spectra and are labeled A and B on the graph. The ground-state resonances A1 and B1 in NiMeOH are separated in field by $\sim 1 \text{ T}$.

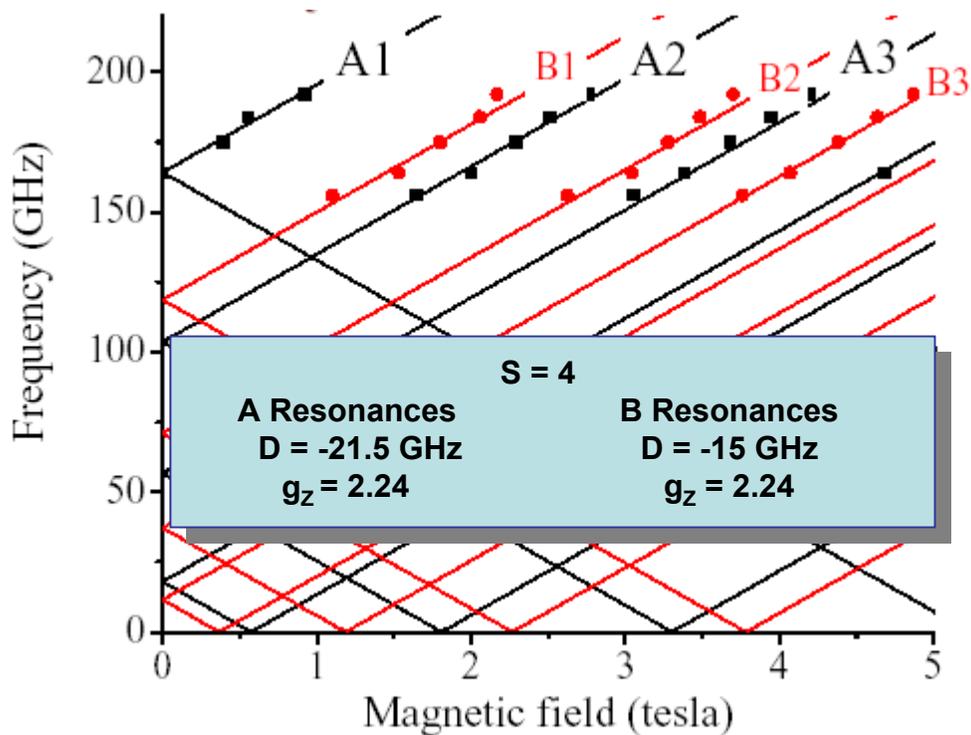


Fig. 14 A and B resonances fit separately to find the total molecular spin and the D and g parameters for NiMeOH.