Reply to Comment on “Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni₄”

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Abstract

Here we respond briefly to a comment on our work in arXiv:cond-mat/0405501.

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A recent Comment \[1\] was posted on cond-mat on our paper entitled “Quantum Coherence between High Spin Superposition States of Single Molecule Magnet Ni$_4$” \[2\]. The main points of this comment can be summarized as follows:

1) That our paper reported experimental studies on the $S = 4$ single molecule magnet Ni$_4$ using a method that combines high sensitivity magnetic measurements with microwave spectroscopy, which was similar to the work posted on cond-mat a few weeks earlier on the $S = 1/2$ molecule V$_{15}$ \[3\]. The implication was that this early posting gives Wernsdorfer claim to being the ‘originator’ of this magnetic measurement method.

2) That pulsed-radiation relaxation experiments, like those we present, do not give directly the spin-lattice relaxation time $T_1$ but the spin-phonon-bottleneck time. As a consequence our finding of an increase of $T_1$ with frequency is not contrary to general ideas.

3) The final claim is that “… all statements concerning the observation of quantum coherence” have not yet demonstrated.

We address these points in the order above.

First, we started planning and discussing these experiments three years ago, including ordering the necessary equipment \[4\]. The experiments on Ni$_4$ were conducted over the last six months. The cited work was presented in an invited talk \[5\] at the APS March Meeting and at an earlier conference \[6\]. Our paper was submitted to Science after the March Meeting (on April 9th 2004, one week before ref. \[3\]) and shortly thereafter to Physical Review Letters. We also note that while our paper was under consideration for publication, an interesting related work by Bal et al. \[7\] appeared. The timing of these publications and talks makes it clear that these papers correspond to independent research carried out in parallel. These experiments and other earlier publications reflect the continued and growing interest of the community in coherent quantum phenomena in SMMs \[8-9\]. The ideas of such combined magnetic/microwave experiments were actively discussed by many in the SMM community \[4-11\], and similar experiments were published some time ago, which investigated quantum superposition states in superconducting quantum interference devices \[12-13\].

In our experiments high sensitivity Hall magnetometry was combined with microwave spectroscopy. We note that Hall magnetometers have recently been demonstrated to have sensitivities of $5 \times 10^5$ spins \[14\] and higher spin sensitivities are certainly possible, with material and device improvements. There is also no fundamental reason that Hall magne-
FIG. 1: Magnetization curves of Ni₄ obtained sweeping at a constant rate, $\alpha = 0.4$ T/min, a longitudinal magnetic field in the presence of different transverse fields. The inset shows the energy of the lowest levels as a function of the longitudinal field.

tometers cannot be used in ultra-fast time resolved measurements ($\sim 10$ GHz), after all, the same semiconductor heterostructure materials used for Hall-magnetometers are used in high-speed circuitry. We note that time resolved magnetic measurements at the nanosecond time scale with micro-SQUIDs have not yet been demonstrated, only fast measurements with SQUIDs specialized for another purpose [15]. The main advantage of Hall magnetometry is the possibility of high sensitivity magnetic measurements over a wide range of temperatures and applied fields (including, very large applied fields).

As alluded to in the Comment, spin-phonon relaxation processes are poorly understood in SMMs (see, for example, ref. [16]). It is certainly true that a spin-phonon-bottleneck can affect the relaxation time in SMMs [18]. We considered this possibility. The small phonon heat capacity and small coupling of sample phonons to the (cryostat) environment can create
an out-of-equilibrium distribution of phonons \[19\]. We have observed this phenomenon in our 
Ni\(_4\) experiments (not reported in ref. \[2\]) as a plateau in the magnetization hysteresis curve
(magnetization lower than its saturation value) after sweeping thought zero field (resonance
\(k = 0\)) in the absence of transverse fields (see fig. 1) \[17\]. The magnetization approaches
its equilibrium value when the longitudinal field is \(\sim 0.15\) T. At this field the separation
between lowest levels is about 30 GHz (see inset in fig. 1). At this frequency, the density
of available phonon modes is apparently sufficient to allow energy relaxation on the time
scale of the hysteresis sweep. Importantly, this plateau gradually disappears with increasing
magnitude of an applied transverse field. This is due to the fact that a transverse field
increases the energy splitting at the resonance, allowing the system to reach a state in which
more and more phonons become available (the distribution of thermal phonons reaches a
maximum at \(3k_B T/h \sim 20 - 40\) GHz).

It is clear from this line of reasoning that since the density of phonon modes increases
with frequency (\(\sim \omega^2\)), the effective relaxation time for a process limited by the phonon-
bottleneck should decrease with increasing radiation frequency (\(\tau \sim 1/\omega^2\)). However, in our
experiments with pulsed microwave fields we observe the opposite behavior (see Fig. 3C
of Ref. \[2\]), which is not understood. Therefore, and as claimed in Ref. \[2\], the observed
dependence of the relaxation time on frequency is opposite that expected based on the
increasing phase space available for phonon generation.

On the last point, we note that our experiments with microwave radiation in Ni\(_4\) have been
carried out in the presence of transverse fields. For this reason, our experiments \[2\] differ
significantly from those discussed above \[3, 7\]. A magnetic field applied perpendicular to
the uniaxial anisotropy axis of the molecules breaks the degeneracy between symmetric and
antisymmetric superpositions of \(S_z\) spin projections, producing an energy splitting between
the states, known as the tunnel splitting. We note that in Refs. \[3, 7\] the energy splitting
between states is linear with applied field and simply corresponds to the Zeeman splittings
between \(S_z\) states. The tunnel splittings are not directly resolved in these experiments.
In our experiments these splittings are directly resolved and reflect the formation of high
spin-superposition states. The lower bound on the coherence time has been determined for
these states to be \(\sim 1\) ns, an order of magnitude higher than the time scale set by radiation
frequency used in the experiment. The observation of quantum coherence between high
spin-states clearly motivates future work in our group and others that will examine the
quantum dynamics in the frequency and time domain, such as Rabi experiments.

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