

A Caveat for Single-Molecule Magnetism: Non-linear Arrhenius Plots

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Single-molecule magnets (SMMs) are molecules that, below a certain temperature (T_B), function as individual nanoscale magnetic particles, exhibiting magnetization hysteresis loops.^[1] As such, they represent an alternative and molecular (bottom-up) route to nanomagnetism, complementing the top-down approach to traditional magnetic nanomaterials.^[2] SMMs also exhibit fascinating quantum behavior such as quantum tunneling of the magnetization (QTM)^[3] and quantum phase interference (QPI),^[4] showing that they are truly mesoscale entities straddling the classical/quantum divide. The barrier causing slow magnetization relaxation arises from a combination of a large ground-state spin (S) and easy-axis anisotropy (negative zero-field splitting parameter, D). The most studied SMMs are the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ family with $S=10$ ground states, and their derivatives,^[5] while in recent years others have been discovered.^[6] Alternating current (ac) magnetic susceptibility studies are a convenient method of assessing whether a compound might be an SMM; frequency-dependent out-of-phase (χ''_M) signals are indicative of the superparamagnet-like properties of an SMM. The variation in signal position with ac frequency can then be used as a source of rate vs T kinetic data, because the χ''_M peak maximum is the temperature at which the angular frequency of the oscillating field equals the rate ($1/\tau$, where τ is the relaxation lifetime) of spin vector reversal. This allows construction of a $\ln(1/\tau)$ vs $1/T$ plot based on the Arrhenius relationship given in Equation (1), the behavior expected of a thermally-activated process over a single barrier:

$$(1/\tau) = (1/\tau_0)\exp(-U_{\text{eff}}/kT) \quad (1)$$

From the slope of the straight line can be obtained the effective barrier to relaxation (U_{eff}), and from the intercept the pre-exponential term ($1/\tau_0$). Adherence to the Arrhenius relationship has been a defining property of a SMM, reflecting the low-dimensional origin of its magnetic properties rather than 3D interactions and long-range magnetic order. Deviations from linearity have been noted in the $\ln(1/\tau)$ vs $1/T$ plot for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot 2\text{MeCO}_2\text{H}\cdot 4\text{H}_2\text{O}$ (**1**) when very high ac frequencies (from several kHz up to 1 MHz) were employed.^[7,8]

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Herein, we show that non-linear Arrhenius behavior is evident even for data collected in the more typical frequency (ν) range (5–1500 Hz), and that the apparent U_{eff} obtained is thus distinctly dependent on the range of data constrained to a linear fit to the Arrhenius equation, giving erroneously large apparent U_{eff} values. This conclusion is supported by comparisons of U_{eff} values with those from high-frequency EPR (HFEPFR) data (U_{EPR}).

The upper limit to the true barrier to magnetization reversal in SMMs can be calculated with knowledge of the spin Hamiltonian parameters, and a reliable method to obtain these is HFEPFR spectroscopy. This gives what we herein refer to as U_{EPR} , and, as stated, this represents a theoretical upper limit to the barrier.^[9] However, this is not necessarily the same as the effective barrier, U_{eff} , measured by kinetic (ac) studies because there may be QTM through higher-energy M_S levels of the ground-state S multiplet, thereby effectively cutting off part of the true barrier.^[3,9] The slope of an Arrhenius plot has thus been an invaluable way to determine U_{eff} experimentally. We have recently been carrying out determinations of U_{EPR} for various SMMs, and have been encountering significant and puzzling differences between them and the corresponding U_{eff} values obtained from linear Arrhenius plots using ac χ''_M vs T data obtained with 5–1500 Hz frequencies; these studies consistently give $U_{\text{eff}} > U_{\text{EPR}}$ rather than the other way around.^[9] We have therefore re-examined data for many compounds, and we have come to the conclusion that even $\ln(1/\tau)$ vs $1/T$ plots constructed using data collected with frequencies < 1500 Hz exhibit noticeable curvature, and that fits to Equation (1) are thus inappropriate!

To better probe this, we have collected data at 25 frequencies lower than 1500 Hz for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{MeOH})_4]\cdot\text{MeOH}$ (**2**),^[10] and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_4]\cdot 4\text{CH}_2\text{Cl}_2$ (**3**),^[11] which (like **1**) crystallize in tetragonal space groups with the Mn_{12} molecules having high (axial, S_4) symmetry. The resulting $\ln(1/\tau)$ vs $1/T$ plot for **2** is shown in Figure 1, and the usual practice of fitting this to a straight line [Eq. (1)] gives $U_{\text{eff}} = 72.0(5)$ K and $\tau_0 = 4.4 \times 10^{-9}$ s (— in Figure 1, top). However, the fit is clearly not great, owing to the curvature. If it is assumed the high- T (high- ν) data represent a deviation from otherwise linear behavior,^[8] then the low- T data (< 600 Hz) can be fitted to give $U'_{\text{eff}} = 69.5(5)$ K and $\tau_0 = 7.1 \times 10^{-9}$ s (— in Figure 1, bottom); the high- T data (≥ 600 Hz) can themselves also be fitted to Equation (1) to give $U''_{\text{eff}} = 81.4(7)$ K and $\tau_0 = 1.1 \times 10^{-9}$ s (----- in Figure 1, bottom). However, this approach completely ignores the overall curvature, which also makes it impossible to decide objectively where data separation should be made for a two-line fit; this, of course, affects the resulting U'_{eff} calculated from the slope (Supporting Information).

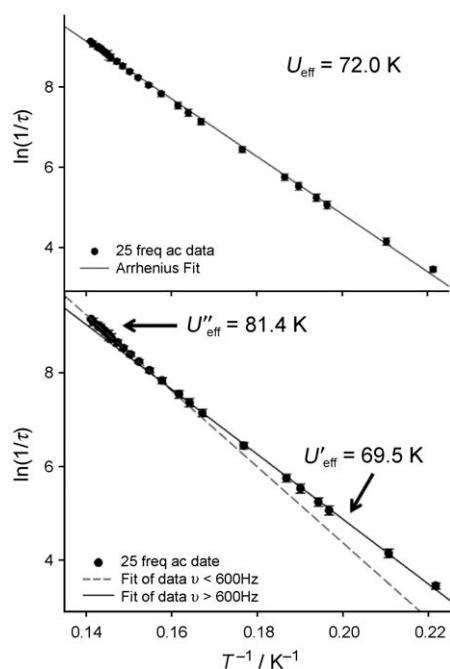


Figure 1. Plot of the natural logarithm of the magnetization relaxation rate vs $1/T$ for **2**. Top: The (—) is the fit of all the data to Equation (1). Bottom: The lines are the separate (two-line) fits of data at > 600 Hz (—) and < 600 Hz (---) to Equation (1), and are extended to emphasize the different slopes.

For comparison, single-crystal HFEPN spectra on **2** were measured in the 50–360 GHz range, with the field along the easy-axis of the Mn_{12} molecule ($B//z$).^[12] Fitting of the resulting data gave $U_{\text{EPR}} = 67.3(13)$ K,^[13] noticeably smaller than $U_{\text{eff}} = 72.0$ K from the linear fit (Figure 1, top), and closer to the $U'_{\text{eff}} = 69.5$ K of the low- ν (low- T) fit. The latter supports the higher- T (higher- ν) data as being the main source of the deviation from the Arrhenius law and the resulting discrepancy between U_{EPR} and U_{eff} . Complex **3** gave similar results: $U_{\text{eff}} = 77.6(4)$ K, $U_{\text{EPR}} = 68.3(13)$ K, $U'_{\text{eff}} = 75.6(5)$ K, $U''_{\text{eff}} = 83.4(4)$ K (Supporting Information). Therefore, the picture that emerges is that fits of the separate data to Arrhenius Equation (1), as one or two linear regions, are either inappropriate, or subjective, or both. Thus, they are unsatisfactory for obtaining reliable U_{eff} values, or ones that can be confidently compared between different researchers who will likely use different frequency sets and thus weight the low- and high-frequency data points differently in a linear fit.

To accommodate the high- T (high- ν) deviations, the modified Arrhenius relationship of Equation (2) was employed, comprising a double-exponential function involving two barriers U_1 and U_2 , and corresponding τ_{01} and τ_{02} , respectively:

$$(1/\tau) = (1/\tau_{01})\exp(-U_1/kT) + (1/\tau_{02})\exp(-U_2/kT) \quad (2)$$

An excellent fit of the $\ln(1/\tau)$ vs $1/T$ data for **2** to Equation (2) was obtained (— in Figure 2, top) with $U_1 = 63(1)$ K, $\tau_{01} = 2.8(6) \times 10^{-8}$ s, $U_2 = 102(4)$ K, and $\tau_{02} = 1.3(7) \times 10^{-10}$ s. U_1 is reasonable for a Mn_{12} SMM and is close to U_{EPR} (67.3 K); as already

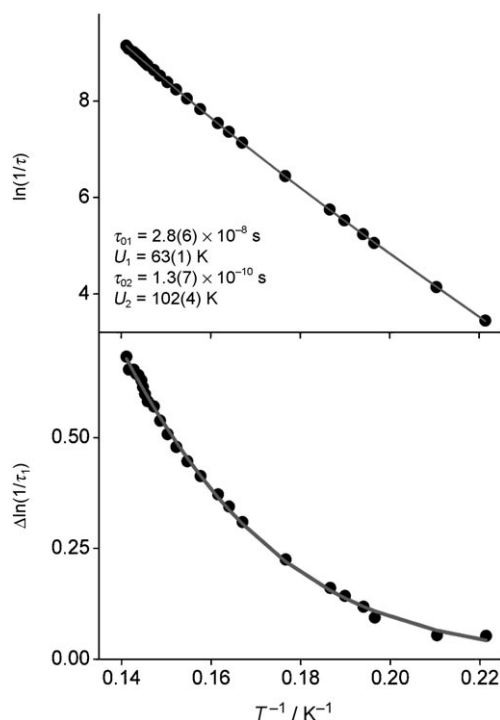


Figure 2. Plot of $\ln(1/\tau)$ vs $1/T$ for **2**. Top: The (—) is the fit to the double-exponential function of Equation (2). Bottom: The deviation $\Delta\ln(1/\tau_1)$ of the data from the straight line given by the first term of Equation (2).

stated, it is reasonable for $U_{\text{eff}} < U_{\text{EPR}}$, due to tunneling below the top of the barrier. In Figure 2 (bottom) is the deviation $\Delta\ln(1/\tau_1)$ of the data from the linear plot resulting from the first term in Equation (2) and the U_1 and τ_{01} values; the deviation is non-zero at all T (ν) values, that is, the second term affects the relaxation kinetics even at the lowest frequencies.

Equation (2) represents a minimal description of what we believe to be behind the curvature of the $\ln(1/\tau)$ versus $1/T$ plots. It consists of a sum of two relaxation processes: the first term corresponds to relaxation within the $S = 10$ ground state, and the second term represents relaxation via excited S states. Under this description, U_1 is the real kinetic relaxation barrier of the $S = 10$ Mn_{12} molecule in its ground state, and U_2 reflects the 'average' excitation energy to a large group of excited states that provide more efficient relaxation pathways, that is, a faster pre-exponential factor $1/\tau_{02}$. Relaxation through excited states will involve processes in which spins within the cluster flip independently of each other, that is, the notion of a rigid spin $S = 10$ breaks down at higher temperatures. There is clearly only a single relaxation process over the $S = 10$ barrier for the rigid spin, whereas there will be a huge number of relaxation pathways involving independent spin-flips. We propose that this is the reason for the significantly faster pre-exponential factor.

While the second term in Equation (2) is phenomenological, the first does accurately reflect the slower relaxation within the ground state. Consequently, Equation (2) correctly captures the low-temperature limiting behavior of the relaxation dynamics, and we thus believe that U_1 provides a reliable estimate of U_{eff}

that is not dependent on factors such as the choice of ac frequencies. The value of U_2 , on the other hand, should not be taken too seriously, although it does agree quite well with the spectroscopically determined locations of excited states.^[11a] A very large $U_{\text{eff}} = 168$ K (and $\tau_0 = 1.0 \times 10^{-11}$ s) obtained from a fit to Equation (1) of $\ln(1/\tau)$ vs $1/T$ data collected in the 100 Hz to 1 MHz frequency range (and T up to 20 K) suggests even faster pathways at higher energies.^[7] Thus, an exact description should probably contain stretched exponentials to capture the high- T behavior.

In summary, the magnetization relaxation of Mn_{12} SMMs does not follow a simple Arrhenius law, even for data collected at < 1500 Hz, due to contributions to the relaxation rate of pathways via excited S states with a larger thermal barrier but much faster spin reversal rates. We have provided a double-exponential modification of the Arrhenius equation that we consider a superior means to obtain the true barrier U_1 of an SMM in its ground state, which also avoids subjective decisions about which data to employ in a linear Arrhenius plot [Eq. (1)] and thus making comparisons between different data sets from different groups and techniques more reliable. Preliminary studies of some other Mn_x SMM families are leading to the same conclusions as for Mn_{12} , that is, non-linear Arrhenius plots at low frequencies are a general property of SMM relaxation kinetics. Note that a modified Arrhenius equation was also needed to fit the spin crossover relaxation rates in light-induced thermal hysteresis studies of certain Fe^{II} compounds, where strong cooperative effects between neighboring molecules lead to self-acceleration effects.^[14] Also note that the present results suggest published U_{eff} values of SMMs obtained from Arrhenius plots using ac susceptibility data are consistently overestimated, in some cases by $\sim 10\%$ or more, for example, the Mn_6 family.^[15,16] It also appears that accurate comparisons of U_{eff} values that have been obtained from ac data using Equation (1) are not possible, unless the data were collected in the same frequency ranges. Without doubt, there is a need for greater theoretical understanding in this area.

Experimental Section

In order to measure the AC magnetic susceptibility of pristine (wet) samples, the crystalline material was first removed from the mother liquor, dried with tissue paper, and rapidly transferred to an analytical balance for accurate weight measurement. Then, within one minute, the crystals were carefully embedded in eicosane within a gelatin capsule in order to ensure retention of the solvent of crystallization. Measurements of the in-phase (χ') and out-of-phase (χ'') AC susceptibilities were made in the 5–1500 Hz frequency range using a Quantum Design MPMS-XL magnetometer.

HFEPN measurements were performed on single crystals at various frequencies in the 50–400 GHz range using a sensitive cavity perturbation technique and a Millimeter-wave Vector Network Analyzer (MVNA) described elsewhere.^[12] The crystals were quickly transferred from the mother liquor and coated with silicone grease in order to avoid solvent loss. The samples were also initially cooled under atmospheric helium gas, with a total transfer time from the mother liquor to the cryostat of just 10–15 min. The mag-

netic field was provided by a 7 T horizontal-bore superconducting magnet associated with a Quantum Design PPMS magnetometer. The horizontal-bore magnet facilitates in-situ rotation of the cavity relative to the applied field. The cavity additionally permits further rotation of the sample about an orthogonal axis (in-situ), thereby enabling collection of data for both easy-axis ($B//c$ -axis) and hard-plane ($B \perp c$ -axis) orientations. Sample alignment is first achieved by locating extrema among plots of spectra recorded at many different field orientations; once aligned, multi-frequency measurements are performed in order to provide data sets which maximally constrain the ZFS parameters.

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- [1] G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, 25, 66.
- [2] a) G. Christou, *Polyhedron* **2005**, 24, 2065; b) R. E. P. Winpenny (Ed.), *Struct. Bond.* **2006**, 122, 262.
- [3] a) J. R. Friedman, M. P. Sarachik, *Phys. Rev. Lett.* **1996**, 76, 3830; b) W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature* **2002**, 416, 406.
- [4] a) W. Wernsdorfer, R. Sessoli, *Science* **2000**, 287, 2417; b) W. Wernsdorfer, M. Soler, G. Christou, D. N. Hendrickson, *J. Appl. Phys.* **2002**, 91, 7164.
- [5] R. Bagai, G. Christou, *Chem. Soc. Rev.* **2009**, 38, 1011, and refs therein.
- [6] a) L. F. Jones, A. Prescimone, M. Evangelisti, E. K. Brechin, *Chem. Commun.* **2009**, 2023; b) T. C. Stamatatos, S. J. Teat, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2009**, 48, 521; c) R. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y.-F. Song, D. L. Long, E. Burkholder, M. Murrie, P. Kogerler, E. K. Brechin, L. Cronin, *Angew. Chem.* **2008**, 120, 5691; *Angew. Chem. Int. Ed.* **2008**, 47, 5609; d) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo, A. Gaita-Arino, *J. Am. Chem. Soc.* **2008**, 130, 8874; e) V. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, A. K. Powell, *Chem. Eur. J.* **2008**, 14, 3577; f) A. K. Boudalis, Y. Sanakis, J. M. Clemente-Juan, B. Donnadieu, V. Nastopoulos, A. Mari, Y. Coppel, J. P. Tuchagues, S. P. Perlepes, *Chem. Eur. J.* **2008**, 14, 2514; g) J. P. Costes, S. Shova, W. Wernsdorfer, *Dalton Trans.* **2008**, 1843; h) P. H. Lin, T. J. Burchell, R. Clerac, M. Murugesu, *Angew. Chem. Int. Ed.* **2008**, 47, 8848; *Angew. Chem.* **2008**, 120, 8980; i) B. Moubaraki, K. S. Murray, T. A. Hudson, R. Robson, *Eur. J. Inorg. Chem.* **2008**, 4525; j) T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem.* **2008**, 120, 6796; *Angew. Chem. Int. Ed.* **2008**, 47, 6694; k) L. Lecren, W. Wernsdorfer, Y. G. Li, A. Vindigni, H. Miyasaka, R. Clerac, *J. Am. Chem. Soc.* **2007**, 129, 5045; l) S. Accorsi, A. L. Barra, A. Caneschi, G. Chastanet, A. Cornia, A. C. Fabretti, D. Gatteschi, C. Mortalo, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* **2006**, 128, 4742; m) R. Bagai, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2007**, 129, 12918; n) M. Shanmugam, G. Chastanet, T. Mallah, R. Sessoli, S. J. Teat, G. A. Timco, R. E. P. Winpenny, *Chem. Eur. J.* **2006**, 12, 8777; o) C. M. Zaleski, E. C. Depperman, C. Dendrinou-Samara, M. Alexiou, J. W. Kampf, D. P. Kessissoglou, M. L. Kirk, V. L. Pecoraro, *J. Am. Chem. Soc.* **2005**, 127, 12862.
- [7] R. Blinc, B. Zalar, A. Gregorovic, D. Arcon, Z. Kutnjak, C. Filipic, A. Levstik, R. M. Achey, N. S. Dalal, *Phys. Rev. B* **2003**, 67, 094401.
- [8] M. A. Gomes, M. A. Novak, R. Sessoli, A. Caneschi, D. Gatteschi, *Phys. Rev. B* **1998**, 57, 5021.
- [9] G. Redler, C. Lampropoulos, S. Datta, C. Koo, T. C. Stamatatos, N. E. Chakov, G. Christou, S. Hill, *Phys. Rev. B*, arXiv:0907.4434.
- [10] a) W. Wernsdorfer, M. Murugesu, G. Christou, *Phys. Rev. Lett.* **2006**, 96, 057208, 1; b) S. Hill, N. Anderson, A. Wilson, S. Takahashi, N. E. Chakov, M. Murugesu, J. M. North, N. S. Dalal, G. Christou, *J. Appl. Phys.* **2005**, 97,

- 10m510; c) S. Hill, N. Anderson, A. Wilson, S. Takahashi, K. Petukhov, N. E. Chakov, M. Murugesu, J. M. North, E. del Barco, A. D. Kent, N. S. Dalal, G. Christou, *Polyhedron* **2005**, *24*, 2284; d) A. G. Harter, C. Lampropoulos, M. Murugesu, P. Kuhns, A. Reyes, G. Christou, N. S. Dalal, *Polyhedron* **2007**, *26*, 2320; e) A. L. Barra, A. Caneschi, A. Cornia, D. Gatteschi, L. Gorini, L. P. Heiniger, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **2007**, *129*, 10754.
- [11] a) K. Petukhov, S. Hill, N. E. Chakov, G. Christou, *Phys. Rev. B* **2004**, *70*, 054426; b) N. E. Chakov, S. C. Lee, A. G. Harter, P. L. Kuhns, A. P. Reyes, S. O. Hill, N. S. Dalal, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2006**, *128*, 6975.
- [12] a) M. Mola, S. Hill, P. Goy, M. Gross, *Rev. Sci. Instrum.* **2000**, *71*, 186; b) S. Takahashi, S. Hill, *Rev. Sci. Instrum.* **2005**, *76*, 023114.
- [13] C. Lampropoulos, J. Lawrence, A. G. Harter, W. Wernsdorfer, S. O. Hill, N. S. Dalal, K. A. Abboud, G. Christou, in preparation.
- [14] a) V. A. Money, C. Carbonera, J. Elhaik, M. A. Halcrow, J. A. K. Howard, J.-F. Letard, *Chem. Eur. J.* **2007**, *13*, 5503–5514; b) C. Enachescu, R. Tanasa, A. Stancu, G. Chastanet, J.-F. Letard, J. Linares, F. Varre, *J. Appl. Phys.* **2006**, *99*, 08J504.
- [15] a) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 2754; b) S. Datta, E. Bolin, C. J. Milios, E. K. Brechin, S. Hill, *Polyhedron* **2009**, *28*, 1788; c) C. J. Milios, A. Vinslava, P. A. Wood, S. Parsons, W. Wernsdorfer, G. Christou, S. P. Perlepes, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 8; d) C. J. Milios, A. Vinslava, W. Wernsdorfer, A. Prescimone, P. A. Wood, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 6547; e) C. J. Milios, R. Inglis, R. Bagai, W. Wernsdorfer, A. Collins, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *Chem. Commun.* **2007**, 3476; f) C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 12505; g) S. Carretta, T. Guidi, P. Santini, G. Amoretti, O. Pieper, B. Lake, J. van Slageren, F. El Hallak, W. Wernsdorfer, H. Mutka, M. Russina, C. J. Milios, E. K. Brechin, *Phys. Rev. Lett.* **2008**, *100*, 157203.
- [16] More examples will be presented in the full paper of this work.

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