

On the ^{169}Tm NMR line shape and local-field distribution in dilute $LiY_{0.98}Tm_{0.02}F_4$: Monte Carlo analysis

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A microscopic Monte Carlo analysis of the ^{169}Tm NMR line shape in dilute $LiY_{0.98}Tm_{0.02}F_4$ is presented. The random occupation of rare-earth lattice sites by Tm^{3+} ions is treated explicitly, and the distribution of dipolar local fields at the resonant ^{169}Tm nuclei is calculated for 5×10^6 independent configurations. It is shown that, in the 2 % diluted system, the nuclear magnetic resonance spectrum is strongly non-Gaussian. Instead of a single smooth line, the calculated profile consists of a dominant central resonance produced by relatively isolated thulium ions and weak satellite components arising from rare close Tm–Tm configurations. This discreteness strongly affects the interpretation of the anomalously large linewidth reported for $\mathbf{H}_0 \parallel [001]$. In particular, the global second moment is found to be highly sensitive to the far wings of the distribution and therefore does not characterize the intrinsic width of the main spin ensemble. The full width at half maximum of the central peak provides a more physically transparent measure of the linewidth in the dilute limit. The calculated angular dependence reproduces the strong anisotropy associated with the van Vleck response of Tm^{3+} ions and supports a microscopic reinterpretation of the observed broadening in terms of conventional dipolar local fields in a spatially disordered rare-earth sublattice.

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Rare-earth dielectric crystals of the $LiYF_4$ family doped with non- Kramers rare-earth ions are convenient model systems for studying hyperfine-enhanced nuclear magnetic resonance in van Vleck paramagnets. In $Li(Y_{1-x}Tm_x)F_4$, the electronic ground state of Tm^{3+} is split by the crystal field, and the field-induced electronic magnetic moment strongly enhances the effective magnetic field acting on the ^{169}Tm nucleus. This makes the ^{169}Tm nuclear magnetic resonance (NMR) line very sensitive to weak changes in the local magnetic environment. Recent spin-echo measurements on dilute $Li(Y_{0.98}Tm_{0.02})F_4$ revealed a pronounced anisotropy of the linewidth and relaxation rates with respect to the crystallographic axes, including an apparently anomalous broadening for the external magnetic field close to the [001] direction [1]. The reported linewidth was much larger than one would naively expect by comparing the 2% diluted crystal with concentrated $LiTmF_4$ [2, 3]. This observation motivates a microscopic reconsideration of what is meant by linewidth in a strongly diluted rare-earth sublattice.

The central point is that a 2 % thulium subsystem is not a continuous magnetic medium. Most ^{169}Tm nuclei are nearly isolated, whereas a small but important fraction has another Tm^{3+} ion in a close coordination shell. These rare local configurations produce much larger dipolar shifts than the typical environment. Therefore, the NMR profile cannot in general be reduced to a single Gaussian line characterized only by the van Vleck second moment M_2 [4, 5]. Since M_2 weights the spectrum as $\Delta\nu^2$, it is intrinsically sensitive to weak far wings and satellites. In a dilute lattice this can make the root-mean-square width describe rare pair configurations rather than the central resonance formed by the majority of nuclei.

To test this idea, the local-field distribution was calculated by a direct Monte Carlo simulation of the diluted rare-earth sublattice. The $LiYF_4$ host was represented by the tetragonal scheelite lattice with $a = 5.16$ Å, $c = 10.73$ Å, and four rare-earth sites per unit cell. A central Tm^{3+} ion was placed at the observed ^{169}Tm nucleus, and surrounding rare-earth sites inside a spherical cluster of radius $R_{\text{cutoff}} = 40$ Å were independently occupied by Tm^{3+} ions with probability $p = 0.02$. The cluster contains about 3.8×10^3 rare-earth positions, i.e. approximately 75 Tm^{3+} ions on average. This radius is sufficient for the present purpose because the dipolar field scales as r^{-3}, whereas the contribution to the second moment scales as r^{-6}; the remaining variance from shells outside radius R decreases as R^{-3}. To

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suppress artificial boundary shifts of the first moment, the cluster was constructed with inversion symmetry.

For each random configuration the secular part of the dipolar local-field sum was evaluated as

$$G = \sum_{j=1}^{N} \sigma_j \frac{3\cos^2\alpha_j - 1}{r_j^3}, \quad (1)$$

where $\sigma_j = 1$ or 0 denotes the occupation of the j-th rare-earth site by Tm^{3+}, r_j is the distance from this site to the observed nucleus, and α_j is the angle between $\mathbf{r}_j$ and the external magnetic field $\mathbf{H}_0$. The angular dependence of the hyperfine-enhanced ^{169}Tm response was introduced through the phenomenological factor

$$\Delta H(\theta) \propto G(1 + 15\cos^2\theta), \quad (2)$$

where θ is the angle between $\mathbf{H}_0$ and the tetragonal [001] axis. The magnetic field was rotated in the (010) plane. The simulated distribution was scaled to the experimental linewidth near $\theta = 0°$ reported in [1]; linewidths are given in kHz/Oe, i.e. as frequency widths normalized by the external field.

The simulations show that the dilute-system line is strongly non-Gaussian. The main resonance is a relatively narrow central peak produced by nearly isolated thulium nuclei, while weak satellites originate from rare close Tm^{3+}–Tm^{3+} configurations. These satellites may have low intensity, but their large frequency offsets strongly affect the integral second moment. Thus, the apparently giant linewidth obtained from an M_2-type analysis should not be interpreted as homogeneous broadening of the entire ^{169}Tm ensemble. It is more accurately viewed as a measure of the full local-field distribution, including rare extreme configurations. For the majority spin ensemble, a more transparent quantity is the full width at half maximum of the central peak.

The calculated angular dependence of the central-peak full width at half maximum is shown in Fig. 1. The linewidth decreases monotonically as the magnetic field is rotated from $\mathbf{H}_0 \parallel [001]$ toward $\mathbf{H}_0 \perp [001]$. This trend follows the anisotropy of the hyperfine-enhanced thulium response and agrees with the qualitative behavior observed experimentally [1]. At the same time, the calculation changes the physical interpretation of the broadening. The large global width is not evidence for a new exotic relaxation channel by itself; it is largely a consequence of applying a continuous-line second-moment formalism to a discrete, configuration- resolved dilute lattice. This conclusion is consistent with the known limitations of second moments in dilute dipolar systems [6–8].

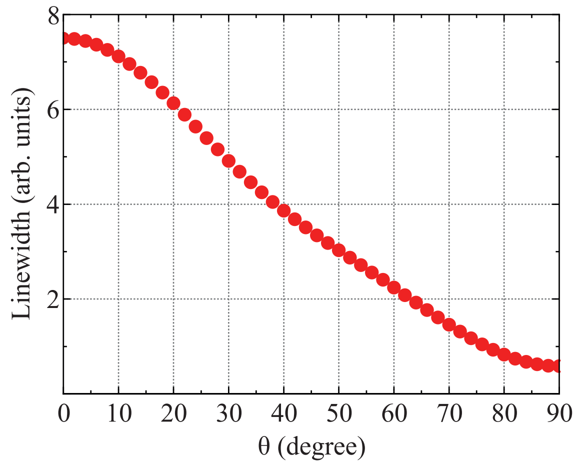

Fig. 1. (Color online) Angular dependence of the ^{169}Tm NMR linewidth in $Li(Y_{0.98}Tm_{0.02})F_4$. Symbols denote Monte Carlo results scaled to the experimental linewidth; the line is a guide to the eye. The plotted quantity is the full width at half maximum of the central component rather than the global second-moment width

The comparison with concentrated $LiTmF_4$ also becomes less paradoxical in this picture. In the concentrated limit, close rare-earth neighbors are no longer rare events: many local configurations overlap, the discrete satellites merge, and the line approaches a continuous broadened profile. In that regime the Gaussian approximation and the second moment become physically meaningful again. In the 2 % crystal, however, the same formal quantity is dominated by statistically uncommon Tm–Tm pairs. The present calculation therefore reconciles the anomalous experimental linewidth with standard dipolar physics by separating the central resonance from the pair-induced wings.

The model intentionally isolates the Tm–Tm contribution to the local field. In the real crystal, the abundant ^{19}F nuclei, together with ^{7}Li and ^{89}Y, provide an additional nuclear dipolar bath. This background should broaden and smooth the calculated profile, and it must be included in a full quantitative theory of T_2. Nevertheless, it does not remove the main conclusion: in dilute $Li(Y_{0.98}Tm_{0.02})F_4$, the ^{169}Tm NMR line shape is intrinsically structured, and the central-line full width at half maximum is a more physically useful measure of the linewidth than the global second moment when discussing the spin ensemble that dominates the echo signal.

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Conflict of interest. The author of this work declares that he has no conflicts of interest.

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