Brief Reports

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Slowly fluctuating random strains in the excited-state Jahn-Teller system $TmPO_4$

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A slight magnetic field dependence in the electron-paramagnetic-resonance fine-structure spectrum of Gd^{3+} in $TmPO_4$ is observed and explained in terms of slowly fluctuating magnetic-field-induced moments in the dynamic random Jahn-Teller-split excited states of Tm^{3+}.

$Tm^{3+}(4f^{12}, {}^3H_6)$ ions in the tetragonal zircon structured $TmPO_4$ have nondegenerate ground states.[1] Because of this nondegeneracy, $TmPO_4$, unlike $TmVO_4$ (Ref. 2) and $TmAsO_4$ (Ref. 3), does not undergo a cooperative Jahn-Teller phase transition.[4–6] However, the first excited state of Tm^{3+} in $TmPO_4$ is a doublet which is only ~44 K away.[1] The occupation of this doublet causes dynamic random Jahn-Teller effects.[7]

$Gd^{3+}(4f^7, {}^8S_{7/2})$ dopants can be used as electron-paramagnetic-resonance probes to detect these effects. This possibility is brought about in three steps: (a) Each Tm^{3+} doublet is split at a given time by the Jahn-Teller effect and is nonmagnetic in the absence of a magnetic field. (b) An applied magnetic field, needed to observe the Gd^{3+} resonance, induces a magnetic moment in the split doublet which is dependent on the magnitude and the direction of the field. (c) The induced moments of the Tm^{3+} ions produce line broadenings in the fine-structure spectrum of the Gd^{3+} ions. As a result of the magnetic field dependence of the Tm^{3+} induced moments, the broadening in the Gd^{3+} spectrum will be field dependent.[8,9]

The observation of the magnetic field dependence in the Gd^{3+} fine structure is possible if the fluctuations of the random strains are sufficiently slow with respect to the measurement time. For systems which have degenerate ground levels, the fluctuations are slow near the phase transitions and the field dependences are clearly observable.[8,9] For $TmPO_4$, however, the effect is very small since the Jahn-Teller interactions are due to the excited states which have relatively short lifetimes. In our previous experiments,[4] the Gd doping levels were ~1000 ppm and the Gd-Gd interactions caused the lines to be too broad for the detection of this very small effect.

We have now looked at samples with ~10- and 100-ppm Gd which allow much more precise measurements. The X-band EPR spectrum of 100-ppm $TmPO_4$: Gd at 60 K with the magnetic field along the c axis is shown in Fig. 1, and the temperature dependences of the seven fine-structure lines are shown in Fig. 2 for the temperature range $4.5 \leq T \leq 78$ K.

At low temperatures, all lines are of about the same widths (~20 G) for both doping levels of 10- and 100-ppm Gd. The equality of the widths for the two doping levels indicates that the remnant Gd-Gd interactions have been practically eliminated as important sources of line broadening. The low-tem-

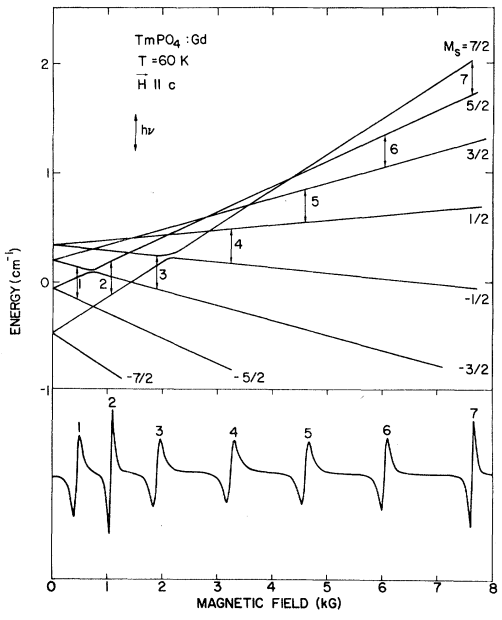

FIG. 1. Energy levels and fine-structure spectrum of $TmPO_4$ (100-ppm Gd) at 60 K with the magnetic field along the c axis.

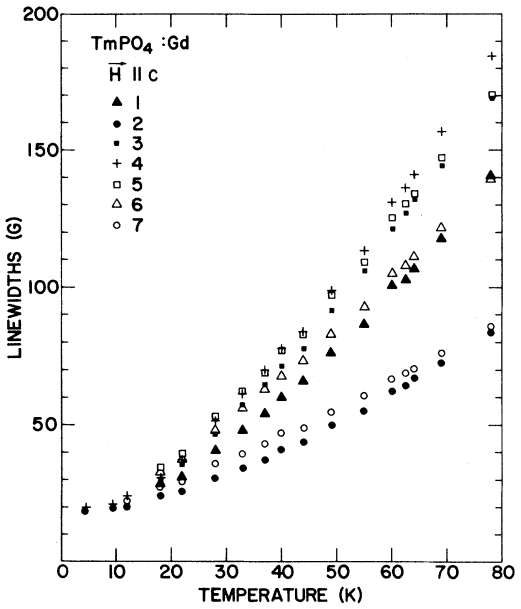

FIG. 2. Temperature dependence of the fine-structure linewidths. Numbers 1 to 7 refer to the lines shown in Fig. 1.

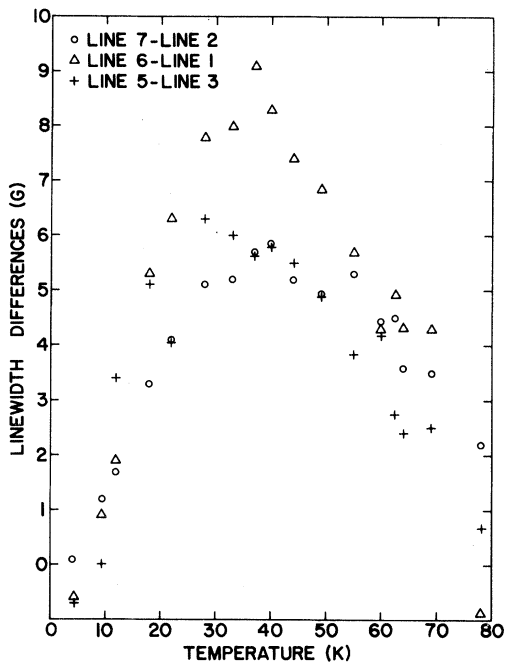

FIG. 3. Temperature variations of the differences between the widths of the lines shown in Fig. 1.

perature linewidths are about twice as large as the Gd^{3+} linewidths in the diamagnetic[10–12] YPO_4. The latter are caused by the hyperfine interactions with ^{155}Gd and ^{157}Gd nuclei and direct superhyperfine interactions with the ligand nuclei. The extra widths of Gd^{3+} lines in $TmPO_4$ are probably due to the *indirect* superhyperfine interactions[13,14] of Gd^{3+} with the ^{169}Tm nuclei through the magnetic polarization of the Tm^{3+} electronic states. The extent of this effect cannot be precisely calculated as the wave functions of Tm^{3+} in $TmPO_4$ are not known.

At the highest temperature used (78 K), lines 2 and 7 in Fig. 1 which, respectively, arise from the transitions $M_s = \frac{7}{2} \rightarrow \frac{5}{2}$ and $M_s = \frac{5}{2} \rightarrow \frac{7}{2}$ are of equal widths; line 1 which arises from $M_s = -\frac{5}{2} \rightarrow -\frac{3}{2}$ is equal in width to line 6 from $M_s = +\frac{3}{2} \rightarrow +\frac{5}{2}$; and line 3 from $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ is equal to line 5 from $M_s = +\frac{1}{2} \rightarrow +\frac{3}{2}$. The relative widths of the seven lines have previously[15] been explained in terms of Gd^{3+} lifetime broadening due to the fast fluctuational fields produced by the Tm^{3+} ions.

In the intermediate-temperature region, a slight magnetic field dependence develops in the Gd^{3+} fine-structure spectrum. To see it, we have plotted in Fig. 3 the temperature variations of the differences between the widths of the lines which are of equal widths in the high-temperature region (i.e., line 7–line 2, etc.) The curves show maxima around 40 K which correspond to the first excited doublet of Tm^{3+} at 44 K. The field dependences in Fig. 3 clearly show that the Tm^{3+} doublets are split by random strains and then magnetic moments are induced in them by the applied magnetic field. Furthermore, the rate of fluctuations of the strains are slow enough to allow the interplay of the Jahn-Teller induced strains and magnetic-field-induced moments to be observable in the time scale of the measurements ($\sim 10^{-9}$ sec). We have previously[9] shown that the random strains produced by the Jahn-Teller interactions of the ground states are time, temperature, and magnetic field dependent. $TmPO_4$ provides the first example in which one can observe similar (but much smaller) effects arising from the excited-state degeneracies.

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