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Jahn-Teller induced random strain effects in $TmPO_4$

F. Mehran and T. S. Plaskett
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

K. W. H. Stevens
Department of Physics, University of Nottingham, Nottingham, Great Britain

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Random strain effects which arise from Jahn-Teller interactions and dominate the high-symmetry phase of cooperative Jahn-Teller systems are also important in $TmPO_4$ although it does not undergo a cooperative Jahn-Teller phase transition. The EPR spectra of $TmPO_4(Gd^{3+})$ are analyzed in terms of these effects.

Nonuniform dynamic strains have been shown to exist in the high symmetry phase of cooperative Jahn-Teller systems.[1-3] We have previously attributed the peculiar temperature variations of the Gd^{3+} EPR spectra in the cooperative Jahn-Teller systems $TmVO_4$ (Ref. 2) and $TmAsO_4$ (Ref. 3) to this phenomenon. These compounds, which have the simple tetragonal zircon structure in the high-symmetry phase, undergo cooperative Jahn-Teller phase transitions to orthorhombic symmetry at low temperatures of[4] 2.1 and 6.1 K,[5] respectively. The transitions are due to the presence of ground electronic doublets of Tm^{3+} and the Jahn-Teller interactions of these doublets with the lattice. Below the transition temperature, the interaction of the electronic doublets with uniform strain is dominant. Above the transition, the interactions of the doublets with phonons dominate and produce nonuniform dynamic strains in the lattice.[2] These electron-phonon interactions can, of course, also arise from the *excited* electronic doublets of Tm^{3+} when they are populated. Indeed the interactions of the excited electronic doublets with phonons have been shown to be much stronger than those of the ground doublets in $TmVO_4$ (Ref. 6) and $TmAsO_4$.[3]

$TmPO_4$, which also has the tetragonal zircon structure, does not undergo a cooperative Jahn-Teller phase transition. The reason is that unlike the other two compounds Tm^{3+} ions in the phosphate do not have degenerate electronic ground states.[7] This may be due to the reversal of the sign of the second order axial crystal field in the phosphate.[8] There are, however, excited electronic doublets at ~44 and 208 K,[7] and the Jahn-Teller interactions of these states with phonons cause nonuniform dynamic strains.

In this paper we report on EPR studies of $TmPO_4(Gd^{3+})$ and show that the temperature variations of the linewidths can be explained in terms of the random-strain model. Because this system does not have a degenerate ground state and does not have a phase transition, the spectra, particularly at low temperatures, are much sharper than those of the previous two systems[2,3]; hence it is much easier to establish the validity of our model in this system.

The experiments were performed at 9 GHz over a temperature range of $1.7 < T < 400$ K. The crystals were grown by the flux method and contained ~1000 ppm of Gd. Throughout the observed temperature range the spectra showed tetragonal symmetry. The fine structure at 6 K with the magnetic field along the *c* axis is shown in Fig. 1. The numbers above each line correspond to the transitions between the energy levels shown in Fig. 2. When the spectrum was fitted to the tetragonal spin Hamiltonian,[2] the second-order parameter B_2^0 was found to be temperature dependent (Fig. 3). The other parameters are temperature independent within the experimental errors:

$$g = 1.992 \pm 0.002 \,,$$

$$B_4^0 = (-8.7 \pm 0.1) \times 10^{-6}\ \mathrm{cm}^{-1} \,,$$

$$B_6^0 = (3.7 \pm 0.4) \times 10^{-8}\ \mathrm{cm}^{-1} \,,$$

$$B_4^4 = (2.2 \pm 0.5) \times 10^{-4}\ \mathrm{cm}^{-1} \,,$$

$$B_6^4 = (-4 \pm 1) \times 10^{-6}\ \mathrm{cm}^{-1} \,.$$

Note that the signs of the crystal-field parameters for Gd^{3+} are identical in $TmPO_4$ and $TmVO_4$,[2] al-

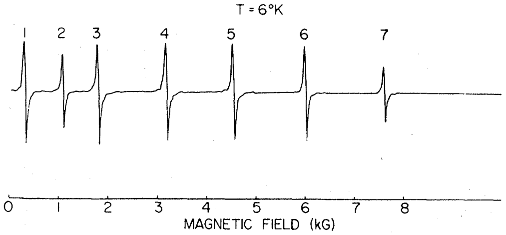

FIG. 1. EPR spectrum of $TmPO_4(Gd^{3+})$ at 6 K with the magnetic field along the *c* axis. The numbers above lines refer to the transitions shown in Fig. 2.

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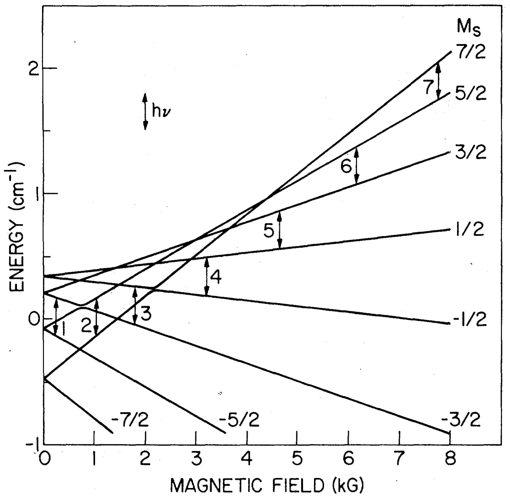

FIG. 2. Energy levels and transitions of $TmPO_4(Gd^{3+})$ at 6 K with the magnetic field along the c axis.

though those of Tm^{3+} reverse[8] in going from $TmPO_4$ to $TmVO_4$. It is possible that the latter statement is not true and a small change in the magnitude of V_2^0 reverses a singlet and a doublet of Tm^{3+} in the phosphate. To clarify this point one needs to know whether the first excited doublet of Tm^{3+} in the phosphate is primarily $M_J = \pm 6$ or $M_J = \pm 5$.

The most interesting part of the observation, as far as the Jahn-Teller interactions are concerned, is the temperature dependence of the linewidths. This is shown in Fig. 4 for the seven lines of the fine structure of Fig. 1 up to a temperature of 100 K. At higher temperatures excessive line broadening reduces the resolution of the spectra and only the highest-field line can be resolved. The temperature dependence of this line up to ~400 K is shown in Fig. 5.

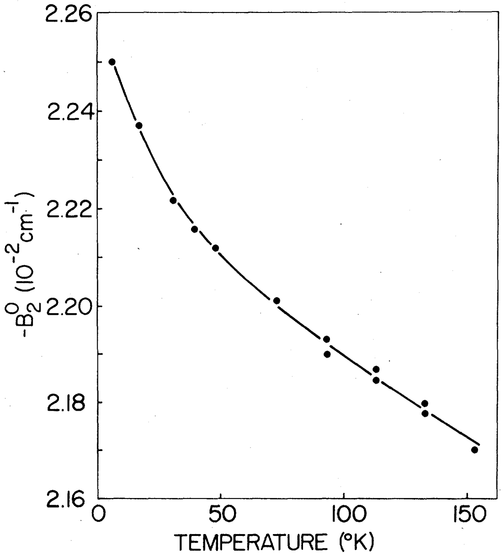

FIG. 3. Temperature variation of the second-order crystal-field parameter B_2^0 of $TmPO_4(Gd^{3+})$.

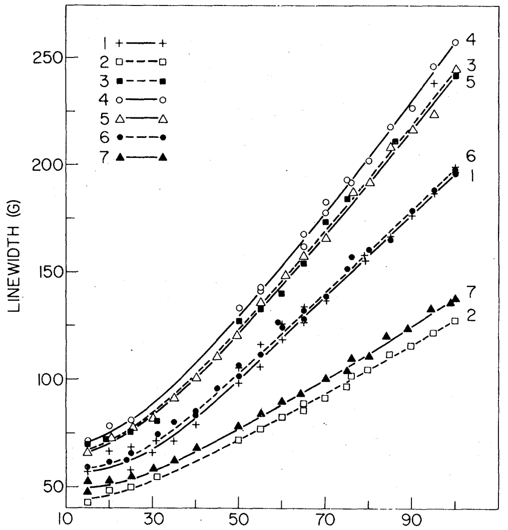

FIG. 4. Temperature variation of linewidths of the fine structure shown in Fig. 1.

We have previously argued[2,3] that there are two major mechanisms contributing to the linewidths of the Gd^{3+} ions in Jahn-Teller hosts in the high-symmetry phase. One is the random dynamic strain effect which causes each Gd^{3+} ion to be locally in an orthorhombic environment which varies from point to point and with time. There is thus a distribution of orthorhombic crystal-field parameters leading to line broadening, depending on the rate of fluctuation. The second mechanism is the

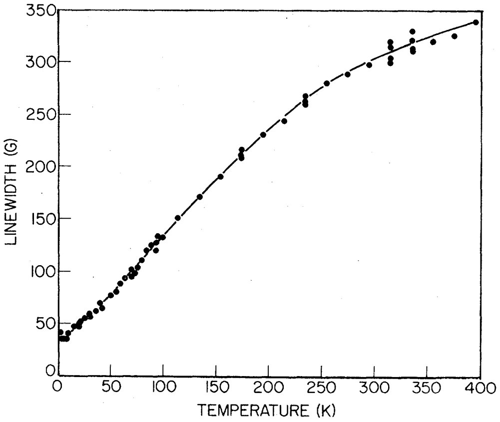

FIG. 5. Temperature variation of the highest-field line of Fig. 1.

dipolar broadening due to the $\mathrm{Gd^{3+}}$-$\mathrm{Tm^{3+}}$ dipolar interactions. This mechanism is magnetic field dependent since in zero field each $\mathrm{Tm^{3+}}$, being in an orthorhombic environment, is split and is nonmagnetic. The dipole moments of $\mathrm{Tm^{3+}}$ ions are therefore induced by the applied magnetic field and therefore are field dependent. (We ignore broadening due to $\mathrm{Gd^{3+}}$ spin-lattice relaxation.) Of these two mechanisms the induced dipolar effect, which is a dominant factor[3] in the low-temperature spectrum of $\mathrm{TmAsO_4(Gd^{3+})}$, seems to be rather unimportant for $\mathrm{TmPO_4(Gd^{3+})}$. This follows from the near-perfect symmetry of the $\mathrm{TmPO_4}$(Gd) spectra of Fig. 1 (i.e., lines 1 and 6 have the same width, etc.). A strong dipolar broadening would cause the spectrum to be highly asymmetric.[3] The only deviation from perfect symmetry occurs for the highest-field line (line 7) which is slightly wider than its counterpart, line 2. The random strain broadening mechanism is, therefore, the only major contributor to the line broadening.

To test this model, we assumed orthorhombic local symmetries for the $\mathrm{Gd^{3+}}$ ions and, in the energy-level calculations, included the effects of the parameter B_2^2 which dominates the orthorhombic crystal-field parameters. The inclusion of the B_2^2 parameter, which has a random distribution over the crystal, gives rise to broadenings of the energy levels. Based on this assumption, we calculated the ratios of the linewidths and compared them to the observed ratios at $T=100$ K. The results are shown in Table I. It is seen that theory and experiment are in agreement within the experimental error for all lines except for the line-7/line-6 ratio. This exception is due to the fact that for the line 7 the dipolar effects, which are ignored in the analysis, are of some importance (Fig. 4). In the previous cases of $\mathrm{TmVO_4}$(Gd)[2] and $\mathrm{TmAsO_4}$(Gd)[3] such clear comparisons between experiment and theory were not possible because the spectra were not sharp enough. One difference between the spectra of $\mathrm{TmPO_4}$(Gd) and those of $\mathrm{TmVO_4}$(Gd) and $\mathrm{TmAsO_4}$(Gd) is that, unlike those of the latter two, the spectra of $\mathrm{TmPO_4}$(Gd) do not show any fluctuational narrowing in the observed temperature range.[2,3] The pseudospin flip rate[2] in this case, therefore, appears to be much lower than in the other two cases.

TABLE I. Theoretical and experimental ratios of linewidths of the fine structure of $\mathrm{TmPO_4(Gd^{3+})}$.

Lines	Theory	Experiment (100 K)
7/6	0.64	0.70 ± 0.03
6/5	0.79	0.81 ± 0.03
5/4	0.93	0.95 ± 0.04
4/3	1.08	1.06 ± 0.04
3/2	1.98	1.91 ± 0.08
2/1	0.64	0.65 ± 0.03

In conclusion, although $\mathrm{TmPO_4}$ does not, due to the lack of a degenerate ground electronic state, undergo a cooperative Jahn-Teller transition it does exhibit the high-symmetry phase properties of the cooperative Jahn-Teller systems. In particular, the random strain effect arising from the Jahn-Teller interactions of the excited electronic doublets with appropriate phonons which dominate the high-temperature phase of the cooperative Jahn-Teller systems also occurs in $\mathrm{TmPO_4}$. In fact, because $\mathrm{TmPO_4}$ does not have a cooperative phase transition, $\mathrm{Gd^{3+}}$ spectra are not complicated by the uniform strain effects and it is therefore a better system for studying the Jahn-Teller induced random strain effects.

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