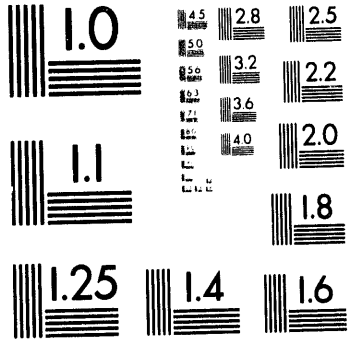
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Spectroscopic Studies of Magnetic Transitions in $TbPO_4$

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Abstract

Rare-earth orthophosphates, RPO_4 (R = Tb to Lu), crystallize in the tetragonal zircon structure in which R occupies sites of D_{2d} symmetry. The R = Tb, Dy, Ho compounds order antiferromagnetically at low temperature with the rare-earth moments parallel to the crystallographic c-axis. In $TbPO_4$ the magnetic transition is accompanied by a cooperative Jahn-Teller effect involving Tb ion-lattice coupling which induces a tetragonal-to-monoclinic distortion of the crystal lattice and a readjustment of the Tb electronic states as required by the lowering of the rare-earth site symmetry. The laser excitation and emission spectra of $TbPO_4$ and 0.1% Tb doped YPO_4 single crystals were studied at temperatures below and above the phase transitions. The line shapes of transitions in the stoichiometric compound are unusually broad and asymmetric whereas those for the dilute compound are sharp. In addition, the $TbPO_4$ spectra show an anomalous temperature dependence near the phase transitions, indicating strong interactions of the rare-earth ions with their environments. A comparison of the optical results with neutron-scattering measurements has been made.

1. Introduction

Rare-earth orthophosphates, RPO_4 (R = Tb to Lu), crystallize in the tetragonal zircon structure (space group $I4_1/amd$) in which four equivalent rare-earth ions in a unit cell occupy sites of D_{2d} symmetry. The magnetic dipole-dipole and superexchange (via the neighboring oxygen atoms) interactions between the rare-earth spins are relatively weak and can be characterized by a total internal effective field of several kG. The low-temperature magnetic properties of these compounds are strongly influenced by the symmetry of the rare-earth low-lying states which are split by crystal-field effects. The Tb, Dy and Ho compounds have doublet ground states dominated by $|J \pm J_M\rangle$ components of large J_M, whereas the Er, Tm and Yb compounds have ground states that are either energetically isolated singlets or Kramers doublets with a highly isotropic spin magnetization density. Consequently, long-range antiferromagnetic ordering has been observed only in the former compounds with Néel temperatures T_N = 2.28, 3.4 and 1.39 K for $TbPO_4$, $DyPO_4$ and $HoPO_4$, receptively.[1-3] The antiferromagnetic phase has a simple two-sublattice structure with the rare-earth magnetic-moment direction parallel/antiparallel to the crystallographic c-axis. Many magnetothermal properties, such as the magnetic susceptibility and heat capacity, can be adequately described by either a three-dimensional Ising model[4,5] or a molecular theory[6].

$TbPO_4$ differs from the other two antiferromagnets in the occurrence of an additional Jahn-Teller transition at 2.15 K where Tb ion-lattice coupling induces a distortion of the tetragonal lattice to monoclinic structure and a tilting of the Tb moments away from the tetragonal c-axis in the (110) plane.[7-9] A number of investigations, both experimental and theoretical, have previously been undertaken in attempts to understand the intriguing properties of $TbPO_4$. In particular, interpretation of the optical absorption and emission spectra as well as electronic Raman-scattering data of $TbPO_4$ are complicated by the unusually broad transitions and asymmetric line shapes. Since the excited states of Tb^{3+} ions in a variety of materials are known to participate in various energy transfer processes involving excitonic fluorescence,

relaxation and dispersion induced by magnetic exchange interactions,[10-13] we have performed optical absorption and emission as well as neutron-scattering experiments on both single-crystal and powder samples of $Tb_xY_{1-x}PO_4$ in attempt to clarify the Tb-Tb interactions at low temperatures. This paper reports the magnetic transitions within the Tb^{3+} $^7F_6$ ground multiplet and electronic transitions between the $^7F_6$ and $^5D_4$ multiplets in both the paramagnetic and antiferromagnetic phases of the $Tb_xY_{1-x}PO_4$ ($x = 0.01$ and 1) compounds.

II. Experimental Details

Single crystals of $TbPO_4$ and 0.1 % Tb: YPO_4 were grown by dissolving and reacting the appropriate rare-earth oxides in molten lead pyrophosphate at high temperature[14] and polycrystalline powder of $TbPO_4$ were prepared by the technique of precipitation from molten urea[15]. The samples were examined by x-ray and neutron diffraction and were found to have the appropriate zircon structure. A tunable dye laser pumped by a pulsed Nd:YAG laser was used in the optical absorption and fluorescence experiments. The laser line width was 0.4 cm^{-1}. Fluorescence emission from the lowest component of the $^5D_4$ multiplet was dispersed by a monochromator and detected by a cooled photomultiplier. Signals from the photomultiplier were averaged using a DEC minicomputer. The optogavanic effect in a uranium-argon hollow cathode lamp was used for wave length calibration of the excitation spectra. The single-crystal samples were mounted in an optical cryostat with the c-axis perpendicular to the incident laser beam. For low temperature measurements ($T \leq 4.2$ K) the samples were immersed into liquid helium and the helium vapor was pumped to reduce the liquid temperature to below the λ point.

The inelastic neutron-scattering measurements were performed using the QENS spectrometer at the Argonne spallation neutron source IPNS. The energy resolution of the QENS spectrometer varies smoothly from about 0.08 meV (0.64 cm^{-1}) at the elastic position to $\approx$0.3 meV (2.4 cm^{-1}) at an energy transfer of 10 meV. Approximately 30 g of polycrystalline

sample of $TbPO_4$, cooled by a conventional helium cryostat, were used in the neutron-scattering experiments.

III. Results and discussion

The $^7F_6 \rightarrow {}^5D_4$ excitation spectra of 0.1% Tb^{3+}: $YbPO_4$ at 8 K obtained with both the σ- (photon electric field E $\perp$ the crystallographic c-axis) and π- (E // c-axis) polarization are shown in Fig. 1. Under the D_{2d} point-group symmetry the Tb^{3+} $^7F_6$ ground multiplet is split by the crystal field into 7 singlets, $2\Gamma_1+\Gamma_2+2\Gamma_3+2\Gamma_4$, and 3 doublets, $3\Gamma_5$, and the $^5D_4$ into 5 singlets, $2\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$, and 2 doublets, $2\Gamma_5$. The Γ_5 doublet ground state has been previously identified by neutron and optical studies[16-18]. The seven observed peaks shown in Fig. 1b can be interpreted as excitations from the Γ_5 ground state to the seven crystal-field split states in $^5D_4$. Selection rules for electric dipole transitions restrict only to $\Gamma_5 \leftrightarrow \Gamma_5$ and $\Gamma_3 \leftrightarrow \Gamma_4$ transitions in the π-polarization and $\Gamma_5 \leftrightarrow \Gamma_{1,2,3,4}$ transitions in the σ-polarization configuration. However, some of the formally forbidden transitions were observed probably due to a leakage of polarization. The energies and line widths of the transitions, determined by nonlinear fits of the data to the reference uranium and argon lines, are listed in Table I. It can be seen that all the optical transitions of the Tb^{3+} ions in the dilute sample are very sharp, given by measured line widths between 0.4 and 0.5 cm^{-1}. Given that the laser line resolution is 0.4 cm^{-1}, inhomogeneous line broadening in this sample then cannot exceed 0.3 cm^{-1}. In addition, intrinsic broadening of the lines due to Tb-Tb interactions and zero-field hyperfine splitting are negligibly small.

We now discuss the optical and neutron spectra of the stoichiometric compound $TbPO_4$. In general, the optical transitions in the 2.2 - 80 K temperature range are unusually broad and the lines are asymmetric. Fig. 2a shows a typical excitation spectra of $TbPO_4$ at approximately 4.2 K in the π-polarization configuration. The transitions from the ground state to the two Γ_5 and the Γ_3 states of the $^5D_4$ multiplet are broadened into three bands with line

widths of more than 10 cm^{-1}. At a lower temperature of 1.5 K we observed that these bands remained to be broad, and new, weak but sharp lines appeared (see Fig. 2b). The assigned transition energies and the estimated line widths for $TbPO_4$ are given in Table II. The small difference in the energies of the levels between the 0.1% Tb:YPO_4 and the stoichiometric $TbPO_4$ samples reflects the somewhat different crystal-field environments in these two materials.

The crystal-field excitations from the ground state to the next four higher states within the $^7F_6$ ground multiplet, measured by neutron scattering at 1.5 and 4.2 K, are shown in Fig. 3. The observed transitions at both 4.2 and 1.5 K are significantly broader than the instrumental resolution. This indicates that the peaks are broadened intrinsically by interactions of the Tb magnetic moments with the environment. In fact, the first three states at 0, 3.8, and 7.8 cm^{-1} at 4.2 K are merged into a band bearing an asymmetric profile. The strong peak at zero energy in the 4.2 K spectrum originates from magnetic elastic scattering within the doubly degenerate Γ_5 ground state. At 1.5 K the degeneracy is lifted by the reduction of site symmetry due to the tetragonal to monoclinic distortion of the lattice. As a results, the elastic intensity diminishes and the spectrum shifts to high energies by approximately 4 cm^{-1}. Incidentally, long-range magnetic ordering have set in and the neutron spectrum represents a measure of the magnon density-of-states. The energy level scheme determined by neutron measurements agrees well with those obtained from emission spectra of the $^5D_4$ Γ_1 to the $^7F_6$ ground multiplet.

The optical and neutron-scattering measurements provided important information regarding the crystal-field effects and magnetic interactions in the $Tb_xY_{1-x}PO_4$ system at low temperatures. In the dilute limit of 0.1% Tb in YPO_4, Tb-Tb interactions are negligible and *single-ion* crystal-field transitions give rise to sharp peaks as observed in the optical spectra at all temperatures. The narrow line widths of these excitations indicate that effects of defect-induced inhomogeneous broadening, zero-field hyperfine splitting of the nuclear spins, and

relaxations of the Tb^{3+} excited states are small. As the Tb concentration increases, the probability for interactions between a pair of Tb^{3+} excited states is enhanced under selective excitation by the laser field in an optical experiment. Such exciton-exciton interactions were indeed observed in $Tb_xY_{1-x}PO_4$ through luminescence studies by Hirano and Shionoya[10], and by Diggle and coworkers[11].

Our optical and neutron-scattering experiments on $TbPO_4$, however, focused on the study of the superexchange interactions between the Tb^{3+} magnetic moments at low temperatures. Such interactions lead to eventually the long-range antiferromagnetic ordering of the Tb^{3+} moments at 2.28 K and a Tb ion-lattice coupling at 2.15 K. However, the exchange interaction must intensify considerably at temperatures precursory of the phase transitions, as manifested by the broadened transitions in the optical and neutron spectra at 4.2 K. The effect of inhomogeneous broadening can be ruled out as the cause because of the appearance of additional narrow peaks at 1.5 K in the optical spectra. The significance of exchange interaction between the Tb ions at $T < 50$ K is also supported by the systematic deviation of the paramagnetic susceptibility, $\chi_{//}$ (with the applied field parallel to the crystallographic c-axis), from the calculated values based solely on single-ion crystal-field effects.[16] At 4.2 K strong exchange interactions induce spin fluctuations which dynamically broaden the otherwise sharp crystal-field levels and reduce the lifetimes of the excitations. Consequently the transition lines are broad and asymmetric. At 1.5 K the Tb^{3+} wavefunctions are determined by the diagonalization of a Hamiltonian which includes the effects of crystal fields and long-range magnetic interactions. In general, the wavefunctions contain many components of $|J\,J_M\rangle$ and vary depending on the spin-wave propagation directions. The broad bands seen in the 1.5 K spectra may be interpreted as magnon-to-optical exciton bands transitions. Such transitions have been found[12,19] previously in $Tb(OH)_3$ and $GdCl_3$ giving rise to broad and asymmetric spectra. The magnon wavefunctions will also modify the selection rules for electric dipole transitions. The additional narrow peaks in the 15 K spectra

probably reflect such enhancement of some transition intensities that are favored by the selection rules. Clearly, further studies of $Tb_xY_{1-x}PO_4$ with intermediate Tb concentrations would help clarify the picture concerning the magnon dispersion relations and energy transfer mechanisms.

Acknowledgment

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Table I. The energies and line widths (in cm^{-1}) of the $^7F_6 \rightarrow {}^5D_4$ transitions of Tb^{3+} in $TbPO_4$ and in YPO_4.

States	$TbPO_4$			0.1%Tb:YPO_4 [a]
	Energies 1.5 K	Energies 4.2 K	Line widths 1.5 K	Energies 8 K
Γ_1	20443.2 (1)	20440	1.0	20431.8 (1)
Γ_2	20447.0 (3)	-	-	20438.6 (1)
Γ_5	20456.0 (5)	20455	10.6	20441.4 (3)
Γ_3	20479.8 (1)	20478	1.8	20461.3 (1)
Γ_1	-	20492	-	20473.4 (1)
Γ_5	20502.5 (5)	20500	9.4	20485.1 (1)
Γ_4	20512.9 (3)	20509	3.4	20496.9 (1)

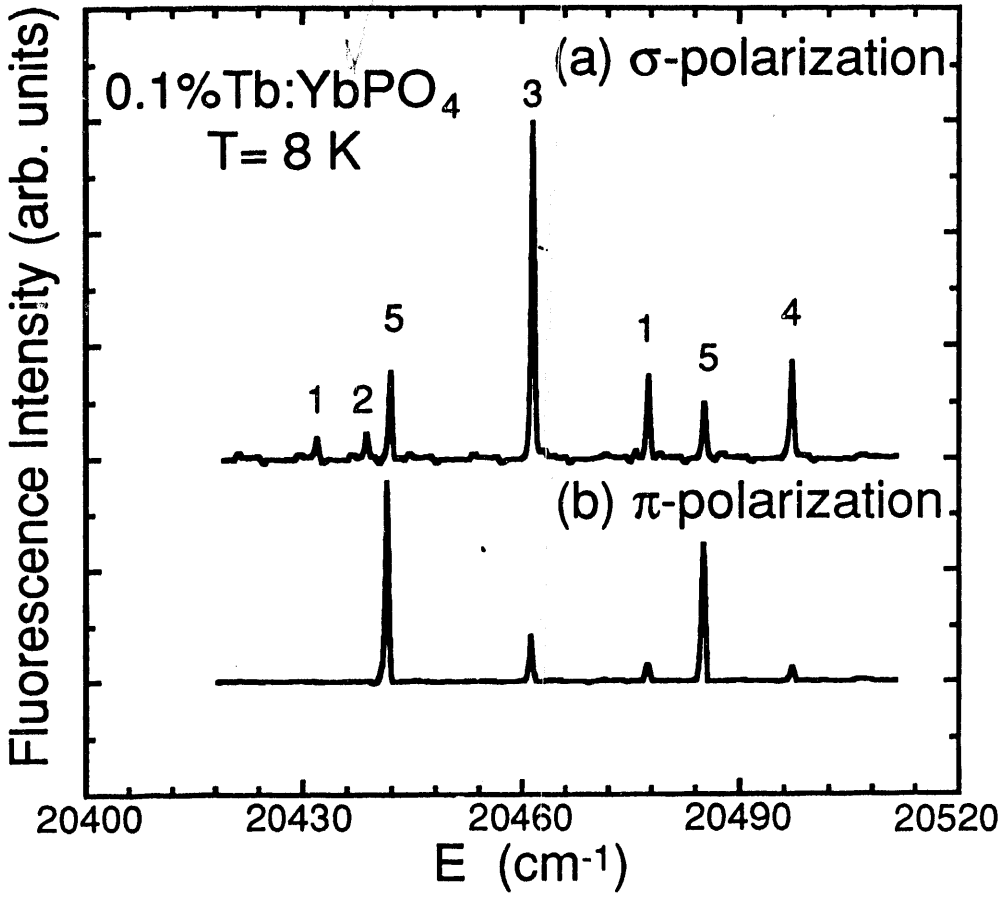
[a] All the line widths are less than 0.3 cm^{-1}.

Figure Captions:

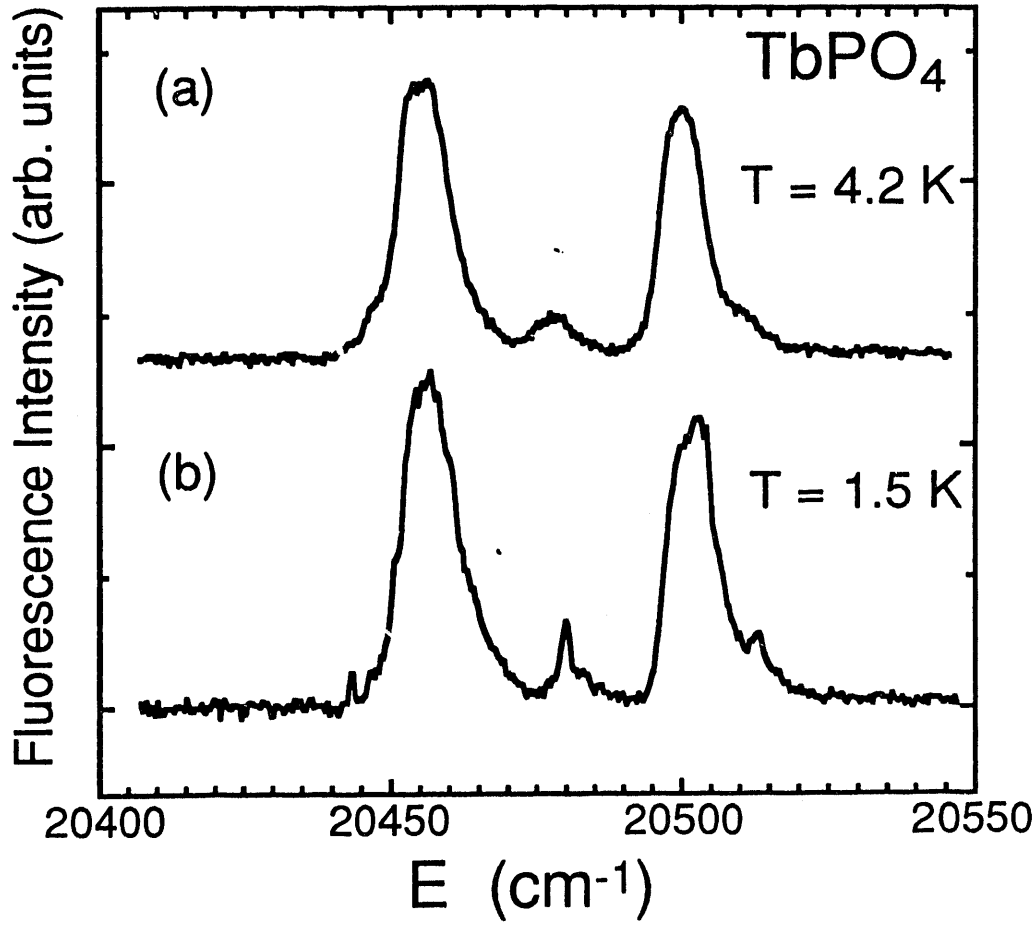
Fig. 1. Laser excitation spectra of the $^7F_6 \rightarrow {}^5D_4$ transitions of Tb^{3+} (0.1%) in YPO_4 at 8 K. (a) σ-polarization and (b) π-polarization. The numbers label the symmetries of the excited states, e.g., 5 denotes a Γ_5 state.

Fig. 2. Laser excitation spectra of the $^7F_6 \rightarrow {}^5D_4$ transitions of Tb^{3+} in $TbPO_4$ in π-polarization. (a) T = 4.2 K and (b) T = 1.5 K.

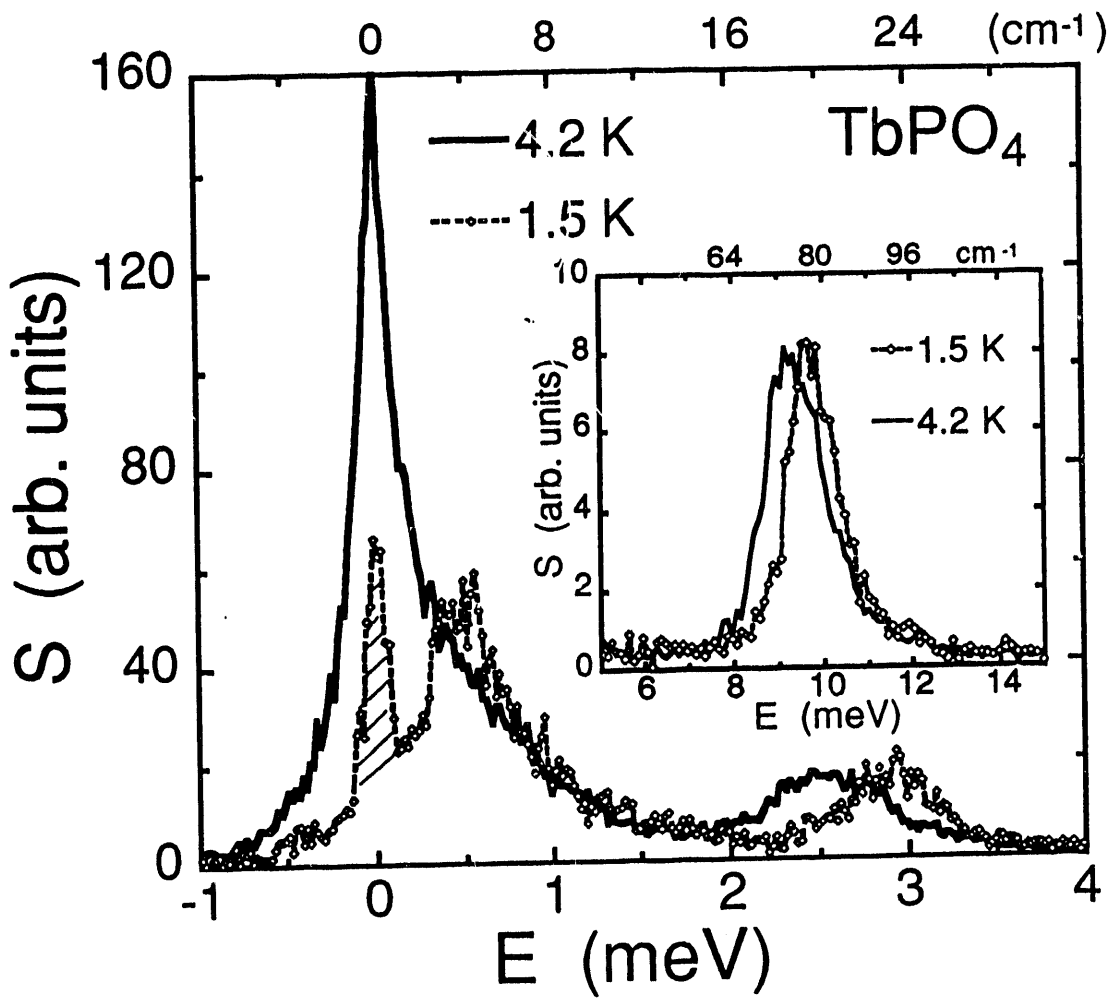
Fig. 3. The low-energy excitation spectra of $TbPO_4$ obtained by neutron-scattering at 4.2 and 1.5 K. The energy resolution of the spectrometer varies smoothly from about 0.08 meV (0.64 cm^{-1}) at the elastic position to ≈0.3 meV (2.4 cm^{-1}) at E = 10 meV. Both spectra contain a residual nuclear elastic-scattering component (shaded area) from the sample and container.



Liu *el at.* HA-10, Spectroscopic Studies of ... 38 MMM Conf. Fig. 1.



Liu *el at.* HA-10, Spectroscopic Studies of ... 38 MMM Conf. Fig. 2.



Liu *el at.* HA-10, Spectroscopic Studies of ... 38 MMM Conf. Fig. 3.

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