Anisotropy of the magnetic properties of the Van Vleck paramagnet $TmPO_4$

V. A. Ioffe,[1] S. I. Andronenko,[1] I. A. Bondar',[1] L. P. Mezentseva,[1] A. N. Bazhan,[2] and C. Bazan[3]
Institute of Physical Problems, Academy of Sciences of the USSR

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The magnetic properties of $TmPO_4$ single crystals have been studied at magnetic fields H from 0 to 60 kOe, at temperatures from 1.7 to 40 K, and also at fields H from 0 to 130 kOe at $T = 4.2$ K. For the first time, an anisotropy of the magnetic moment $M(H)$ has been observed in the basis plane of the crystal in the orientations $\mathbf{H} \parallel [100]$ and $\mathbf{H} \parallel [110]$. This anisotropy arises at $H > 10$ kOe and persists in strong magnetic fields.

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The single crystal of thulium orthosphosphate, $TmPO_4$, of tetragonal symmetry, is a Van Vleck paramagnet with a Jahn-Teller interaction and is currently being studied intensely.[1–10] In a study of the electron paramagnetic-resonance (EPR) spectra of Gd in $TmPO_4$, Mehran *et al.*[1] observed a temperature dependence of the width of the EPR line, which they attributed to dynamic Jahn-Teller distortions, which form an orthorhombic local neighborhood for the rare earth ion. Harley and Manning[2] studied the temperature dependence of the elastic constants c_{66} and c_{44}. They observed a sharp decrease in c_{66} near $T \approx 20$ K and attributed it to a Jahn-Teller coupling of the Tm^{3+} ion with the B_{2g} lattice vibrational mode. Since the elastic constant c_{66} does not reach zero at $T \approx 20$ K, Harley and Manning[2] state that no Jahn-Teller cooperative phase transition occurs in $TmPO_4$. Abdulsabirov *et al.* studied the EPR of Gd^{3+} ions in $TmPO_4$ in magnetic fields up to 20 kOe and observed an anisotropy of the magnetic properties of $TmPO_4$ in strong magnetic fields.

We felt it worthwhile to study the dependence of the magnetic moment of the magnetic field applied to $TmPO_4$ for various orientations of H with respect to the axes of the single crystal. The present experiments were carried out in a vibrating-sample magnetometer[4] developed in the Institute of Physical Problems, at magnetic fields from 0 to 60 kOe and at temperatures in the interval $1.7\ \text{K} < T < 40$ K. We also used a magnetometer developed in the International Laboratory of High Magnetic Fields and Low Temperature (Wroclaw, Poland) at magnetic fields from 0 to 150 kOe at $T = 4.2$ K. The $TmPO_4$ single crystals contained Gd^{3+} and Er^{3+} impurities which were present in the original thulium oxide; the EPR spectra of these impurities were studied in these crystals.[3]

Figure 1a shows the dependence of the magnetic moment on the applied magnetic field H for several orientations of H: Curve 1—along the [100] twofold axis; 2—along the [110] twofold axis; 3—along the [001] tetragonal axis. We see that the dependence $M(H)$ for the orientation $\mathbf{H} \| [100]$ is the same as that in the orientation $\mathbf{H} \| [110]$ in

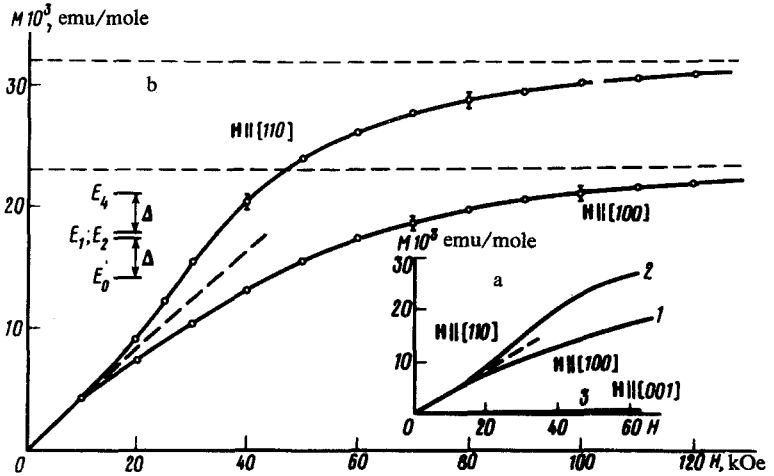

FIG. 1.

magnetic fields up to 15 kOe and is described by $M(H) = \chi H$, where $\chi = 0.38 \pm 0.02$ emu/mole. At magnetic fields $H \geqslant 15$ kOe, the $M(H)$ dependence becomes quite different in the two cases $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$ and is nonlinear in both cases. In the orientation $\mathbf{H}\|[001]$ we observed the linear dependence $M(H) = \chi^* H$, where $\chi^* = (1.5 \pm 0.2) \times 10^{-2}$ emu/mole. Analyzing the magnetization curves $M(H,T)$ for various temperatures, we plotted the temperature dependence of the magnetic susceptibility, $\chi(T)$, for weak magnetic fields, $H < 15$ kOe (Fig. 2a), in the orientation $\mathbf{H}\|[100]$ (curve 2); we also plotted the temperature dependence of the difference $\Delta M(H_0)$ between the magnetic moments $M(H)$ at $H_0 = 50$ kOe for $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$ (Fig. 2b). It can be seen from Fig. 2b that the temperature dependence of the susceptibility and that of the difference between magnetic moments, $\Delta M(H_0)$, for $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$ change in nature over an interval of about 18 K in the temperature T. Figure 1b shows the dependence of the magnetic moment on the $M(H)$ applied to $TmPO_4$ for $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$ at $T = 4.2$ K in magnetic fields up to 130 kOe. We se that the dependence $M(H)$ remains nonlinear in the orientations $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$, and

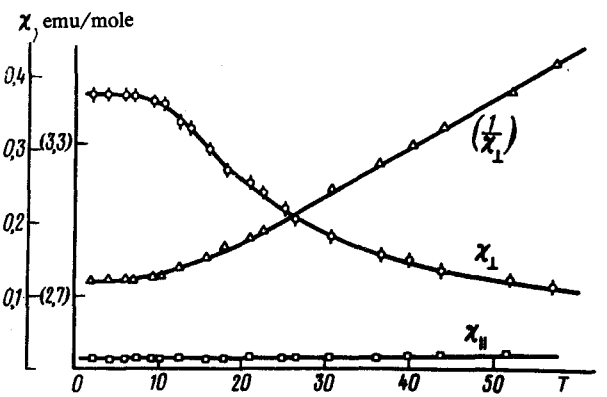

FIG. 2.

$M(H)$ remains anisotropic. It may be that the nonlinear dependence of the magnetic moments, $M(H)$, in the orientations $\mathbf{H}\|[110]$ and $\mathbf{H}\|[100]$ tends toward saturation with increasing magnetic field: $M(H) = M_0$, where $M_0 = (3.2 \pm 0.3) \times 10^4$ emu/mole, and $M(H) = M_0^*$, where $M_0^* = (2.3 \pm 0.3) \cdot 10^4 \sqrt{2}/2 M_0$.

Discussion of Results

In weak magnetic fields, $H < 15$ kOe, $TmPO_4$ single crystals exhibit the unsual properties of a Van Vleck paramagnet. The dependence of the magnetic moment on the applied magnetic field is linear, and the magnetic susceptibility does not depend on the temperature $T < 6$ K. As the temperature is raised, the magnetic susceptibility $\chi(T)$ becomes inversely proportional to the temperature. Curve 2 in Fig. 2 shows the T dependence of $1/\chi$. The dependence $1/\chi(T)$ is seen to be linear at $T > 18$ K. The effecitve $g_\perp$ factor for the magnetic moment in the (001) plane can be determined for $TmPO_4$ with an effective spin $S = \frac{1}{2}$ from the Curie-Weiss law for the suceptibility $\chi(T)$, which incorporates the change in the Van Vleck susceptibility with the temperature which results from the changes in the populations of the ground and lowest excited energy levels. The result is $g_\perp = 10 \pm 1$. Figure 1 shows the $TmPO_4$ energy levels found from optical measurements.[5] According to Ref. 5, the $TmPO_4$ ground state is a singlet; the closest-lying doublet is separated from the ground state by an energy $\Delta \approx 30$ cm^{-1}. Then comes a singlet at a distance $\Delta \approx 30$ cm^{-1}. The following energy levels are separated by $\Delta E \approx 140$ cm^{-1}. In discussing the magnetic properties of $TmPO_4$, we may consider the four nondegenerate electronic levels shown in Fig. 1.

The reason for the anisotropy of the susceptibility in the orientations $\mathbf{H}\|[100]$ and $\mathbf{H}\|[001]$ is that electrons in levels higher than those indicated in Fig. 1 should contribute to the susceptibilities χ^* ($\mathbf{H}\|[001]$) according to the symmetry.[6] The $g_\|$ factor for the magnetic moment in the orientation $\mathbf{H}\|[001]$ can be assumed to be $g_\| \approx 0$ in comparison with the value of the $g_\perp$ factor with $\mathbf{H}\perp[001]$. The electrons at the energy levels Δ and 2Δ contribute to the susceptibility χ ($\mathbf{H}\perp[001]$). The value found by us for the susceptibility χ corresponds to an energy interval $\Delta = 28 \pm 4$ cm^{-1} between the ground and nearest excited levels.

The $TmPO_4$ crystals exhibit an unusual magnetic property: the appearance of the nonlinear dependence $M(H)$ and the appearance of an anisotropy of $M(H)$ in the orientations $\mathbf{H}\|[100]$ and $\mathbf{H}\|[110]$ in fields $H > 15$ kOe. It may be possible to explain this

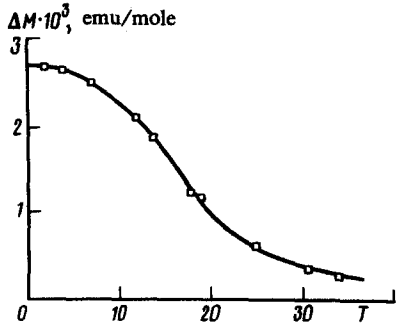

FIG. 3.

behavior by the molecular-field theory with a Jahn-Teller effect which was developed in a review by Gehring and Gehring[7] and in Refs. 8 and 9, for the same four lowest-lying, nondegenerate, electronic states and the Jahn-Teller distortions of the tetragonal $TbVO_4$ lattice.

It can be seen from curve 1 in Fig. 1 that the nonlinearity of the $M(H)$ dependence takes a different form in magnetic fields $H \approx 30$–40 kOe oriented along the [110] axis. The susceptibility $\chi(H)$ reaches its maximum value in these fields. This dependence of the magnetic moment and of the magnetic susceptibility can be explained by assuming, as in Refs. 6 and 10, that the doublet lying nearest the ground singlet, and separated from it by an energy interval $\Delta = 30$ cm^{-1}, is split by the magnetic field. A level intersection occurs at a field $H_c \approx 30$ kOe. For an effective spin of $\frac{1}{2}$ and for a $g_\perp$ factor $g_\perp = 10 \pm 1$, an energy interval $\Delta \approx 30$ cm^{-1} corresponds to an intersection magnetic field $2g_\perp \mu_B S H_c = \Delta$, $H_c \approx 30$ kOe. A possible explanation for the pronounced splitting of the doublet by the magnetic field is that the field $\mathbf{H} \| [110]$ causes a magnetostrictive or Jahn–Teller distortion of the $TmPO_4$ lattice and a change in the crystal field acting on the Tm^{3+} magnetic ion, splitting the doublet. This assumption can be reconciled with the conclusions reached in Refs. 6–10. In a magnetic field $\mathbf{H} \| [100]$ the nonlinear dependence $M(H)$ shown by curve 2 in Fig. 1 has no distinctive features in strong magnetic fields, and the susceptibility falls off smoothly in magnitude. The nonlinear behavior $M(H)$ for $\mathbf{H} \| [110]$ and $\mathbf{H} \| [100]$ in strong magnetic fields can be explained by assuming that the energy levels of the Tm^3 ion in Fig. 1 are shifted by the crystal field and magnetic field and by calculating the shifts of these levels by the magnetic fields $\mathbf{H} \| [110]$ and $\mathbf{H} \| [100]$ (Ref. 11).

A detailed analysis of these experimental results will be published separately.

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[1)]Institute of Silicate Chemistry, Academy of Sciences of USSR, Leningrad.
[2)]Institute of Physical Problems, Academy of Sciences of the USSR, Moscow.
[3)]International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland.

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