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Extensive studies on the low-temperature properties of $TbPO_4$: I. Magnetic measurements

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Abstract. At low temperatures, $TbPO_4$ shows two phases with antiferromagnetic ordering in immediate succession, the upper one with tetragonal and the lower one with monoclinic crystal symmetry. Magnetization and magnetic susceptibility were measured in the region of these phases for different external field directions. One main aspect was to study the anisotropy of the susceptibility for a single-domain crystal in one of the low-symmetry phases. Unexpectedly, it turned out that the susceptibility is isotropic in the basal plane.

1. Introduction

A great deal of experimental and theoretical work has been done on the low-temperature properties of the tetragonal rare-earth compounds with zircon structure (space group $I4_1/amd$, site symmetry $\bar{4}m2$) during the last two decades. Several of these compounds show a structural phase transition as a consequence of a cooperative Jahn–Teller effect, others show a magnetic phase transition and some show both effects. Among these salts, $TbPO_4$ is the one with the most interesting and exceptional features, which, despite repeated efforts, are still not completely understood. The crystal shows two phase transitions very close together. Below $T_{N1} = 2.28 \pm 0.02$ K, a simple two-sublattice antiferromagnet (AF) is formed with the moments parallel to the tetragonal c axis. (The reader who is not familiar with the substance may have a look at the phase diagram of figure 5 of paper III (Müller *et al* 1993).) Below $T_{N2} = 2.13 \pm 0.02$ K, the antiferromagnetic structure is canted off the c axis in a $\{1\,1\,0\}$ plane (still collinear) and the crystal symmetry is lowered at least to monoclinic by a cooperative Jahn–Teller effect (Nägele *et al* 1980), leading to a phase AF′. In external magnetic fields along the c axis, a spin-flop-like phase (SF) is crossed before the saturated paramagnetic phase (PM) is reached. As a consequence of the reduced symmetry, the crystal is usually divided into crystallographic domains. The observed features of the substance depend in a typical way on this domain structure.

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The phase transitions, the magnetic phase diagram and the suspected magnetic structures in the different phases were determined from measurements of the specific heat, magneto-caloric effects (Üffinger and Kasten 1985, Kasten and Üffinger 1985), the linear optical birefringence (Becker *et al* 1985) and the magneto-electric effect (Bluck and Kahle 1988). Spectroscopic investigations were used to ascertain the energy levels of the Tb^{3+} ions in $TbPO_4$ and to calculate the eigenfunctions for the crystal-field components of the ground term $^7F_6$ (Böhm *et al* 1984). The five lowest states, a doublet and three excited singlets, lie very close to each other and determine the properties of the substance even at low temperatures.

For a theoretical description of the observed properties of $TbPO_4$ in the successive phases, different approaches have been proposed. Sivardière (1973) used an effective spin $S = 1$ formalism and, by adopting special values of the coupling constants, he was able to verify the succession of the different phases. But his calculations were based on deficient experimental data. Andronenko *et al* (1984) introduced an interaction with a magnetic-field-induced deformation of the crystal and thereby could quite satisfactorily reproduce their experimental results above 4.2 K. But they did not apply it to the ordered phases. Kasten and Üffinger (1985) handled the full five-level system, but confined the problem to the (110) plane. This method was very successful in explaining the measured specific heat, the magneto-caloric effects (Üffinger and Kasten 1985) and the magneto-electric effect (Bluck and Kahle 1988) at low temperatures for small and medium fields. Nevertheless, it yields unsatisfactory results for our latest experiments.

In this paper, investigations of the magnetization and magnetic susceptibility of $TbPO_4$, measured for different external field directions, are presented. In a second and a third paper (Anderer *et al* 1993, Müller *et al* 1993, henceforth to be referred to as II and III, respectively) measurements of the Faraday rotation and of the linear optical birefringence on this compound will be published. Especially the findings of paper III are surprising since some new combined structural and magnetic phase transitions are found that seem not to be discernible in magnetic measurements. These results require some modification in the theoretical treatment. A new theoretical approach is included in paper III to get further insight into the different low-temperature phases found in the experiments.

2. Experimental details

2.1. Magnetization and AC susceptibility

Measurements of the magnetization M were accomplished with a vibrating-sample magnetometer (PAR FM-159) using a ^{4}He exchange-gas cryostat described by Hülsing *et al* (1979). Temperatures down to 1.2 K (absolute accuracy ±20 mK, short-time stability < 1 mK) and magnetic fields up to 5 T (absolute accuracy ±1.5%, short-time stability < 0.1 mT) were available. The magnetization values were calibrated by means of a nickel probe. Sample vibration (frequency and amplitude) as well as temperature and magnetic field variations were computer-controlled.

The AC susceptibility χ was measured with a mutual induction bridge depicted by Müller *et al* (1982). The amplitude of the AC field was kept at 0.01 mT. Two different coil systems were available, one with its axis parallel, the other perpendicular to the external field B_{ext} to study either the parallel ($\chi_{\parallel}$) or the perpendicular susceptibility

($\chi_\perp$), respectively. Temperature and field regions were about the same as for the magnetization measurements, whereas the accuracy of the measurement was a bit lower. One reason was the difficulty in exactly orienting the crystal. Another was the fact that the thermoresistor for detecting the temperature had to be fixed at some distance from the sample, with the consequence that a seeming hysteresis was observed between up and down sweeps as soon as the temperature was swept too quickly. Thus the absolute accuracy of the temperature measurement was reduced to ±40 mK. Studies at different frequencies in the range 100 Hz to 1 kHz gave no distinguishable variation, and thus a fixed frequency of 111 Hz was used throughout.

2.2. *Test of the method of measuring the perpendicular susceptibility*

To examine the arrangement for investigating $\chi_\perp$, measurements were performed on $DyVO_4$, which likewise crystallizes in the zircon structure. This substance undergoes a Jahn–Teller induced structural phase transition to orthorhombic symmetry at $T_D = 14$ K (Kasten 1980). By this the magnetic moments of the Dy^{3+} ions (and the magnetization and susceptibility, too) become extremely anisotropic with $g_a = 19.0$, $g_b = 0$, $g_c = 0.5$, where a, b, c are the orthorhombic axes. Owing to the reduced symmetry, the crystal is divided into two types of crystallographic domains with their distortions along the respective a directions. The crystal was fixed with one of its tetragonal a axes along the axis of the coil system, i.e. perpendicular to the external field, with the other a axis along the field direction. In measuring $\chi_\perp$ at 4.2 K on a non-premagnetized crystal in a small external field, one finds a relatively high value, which is given by $\chi_\parallel$ of those domains which have their a axis along the axis of the coil system. With increasing field these domains turn over to the other domain type and the crystal finally becomes single-domain with its distortion in the field direction. The value of $\chi_\perp$ drops abruptly at 0.15 T to very small and still decreasing values and goes to zero at about 1 T. Reducing the field strength afterwards, the crystal remains almost single-domain even at zero field. The measured $\chi_\perp$ generally is very small.

2.3. *Samples*

The tetragonal $TbPO_4$ crystals were grown in a $Pb_2P_2O_7$ flux (Hintzmann and Müller-Vogt 1969) under optimized growing conditions (Eigermann *et al* 1978) with low Pb impurity content (< 0.1%). They were of good optical quality and were mounted free of stress in special crystal holders. Samples from different growth batches showed identical results. Thus the presentation in this and in the following papers II and III will concentrate on the findings of a few crystals that are representative of the findings on all of them.

In this publication the findings on four different samples are evaluated. The dimensions and approximate demagnetizing factors of these crystals (in SI units, determined for an ellipsoid with the principal axes equal to the crystal dimensions) are:

sample 1 $a \times b \times c = 0.75 \times 0.75 \times 3.45$ mm^3

$N_a = N_b = 0.475, N_c = 0.05$

(used for the temperature and field dependence of M along c and a)

sample 2 $a \times b \times c = 0.8 \times 0.8 \times 4.5$ mm^3

$N_a = N_b = 0.48, N_c = 0.04$

(temperature and field dependence of M and χ along c, a and x)

sample 3 $x \times y \times z = 1.4 \times 0.1 \times 1.4$ mm^3

$N_x = N_z = 0.01, N_y = 0.98$

(angle dependence of M in the xz plane)

sample 4 $a \times b \times c = 1.0 \times 1.0 \times 1.3$ mm^3

$N_a = N_b = 0.365, N_c = 0.27$

(observation of domains)

Since the substance is distorted in a {1 1 0} plane below T_{N2}, two coordinate systems are used to describe its properties, the crystallographic a, b, c system and an x, y, z system rotated by 45° around the $c \equiv z$ axis, where y is the monoclinic axis while x and z are, strictly speaking, not symmetry axes any more.

3. Experimental results

3.1. Magnetization

The temperature dependence of the magnetization $M(T)$ for fields along c, measured in small steps (step width reduced to 10 mK in the ranges of great curvature), is given in figure 1. With increasing fields the curves become steeper and the jump, which corresponds to the transition out of the AF′ phase, is shifted to lower temperatures. After a maximum, each curve decreases again for increasing temperature, which is the usual paramagnetic behaviour. For fields exceeding 3.0 T, however, the magnetization stays almost constant up to 4.2 K. This is caused by the thermal population of the first excited singlet state, which has a large magnetic moment in high external fields.

The $M(T)$ curves for fields along x and a (not shown) have, in principle, similar shapes. At the same field strength, the absolute values are smaller by a factor of roughly 3; the jump and the following maximum are shifted to higher temperatures, in comparison with those measured with fields along c.

Figure 2 shows the field dependence of the magnetization $M(B)$ for fields along the c, x and a directions, respectively, measured at 1.2 K. The dots are the experimental magnetization versus external field B_{ext}, and the full curves give the demagnetized values versus internal field B_{int}. For fields along c two relatively sharp bends corresponding to the two transitions into the SF and into the PM phases (at about 0.5 T and 1.1 T) are found; for the other two directions only one transition into the PM phase is seen (their field values are approximately in the ratio $1:\sqrt{2}$). It is remarkable that the points measured for fields along x give a vertical jump already without demagnetization and an overhanging to the left after demagnetization. The inset of figure 2, where the experimental points are drawn versus B^x_{ext}, gives an impression of the sharpness of this jump, which could not further be resolved, for

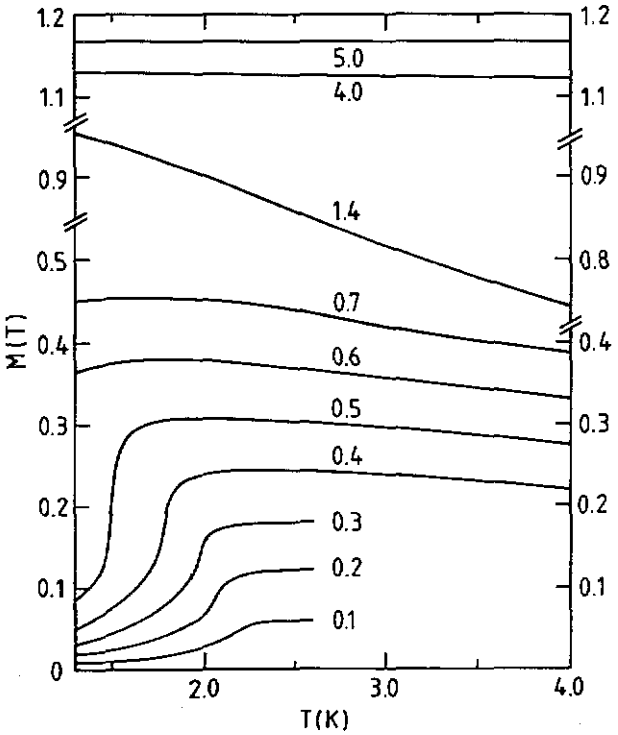

Figure 1. Temperature dependence of the magnetization for fields of different strengths along c, measured on sample 1. The figures on the curves give the respective fields B_{ext} in tesla. Averaged curves are shown. The scattering of the measuring points lies within the width of the drawn lines.

example, by a smaller step width or a variation of the measuring time per point. An attempt at explaining this effect will be given in paper III. Only at 1.95 K for increasing field and at 1.85 K for decreasing field do the demagnetized curves show a vertical jump. At even higher temperatures the increase has always a finite derivative. Hence, the phase transition will change over from first to second order. For fields along c and a, the steep linear increase in the measuring points (dots) is, by the demagnetization, converted into a vertical jump in the full curves. The phase transitions are of first order up to 1.9 K for fields along c and presumably also up to 1.9 K for fields along a. It is noteworthy that the magnetization curves for fields along x and a are almost identical up to about 0.55 T.

Near to the first-order phase transitions, the measured curves show hysteresis for all three field directions. For fields along x and a (curves 2 and 3), figure 2 gives not only the up and down sweeps, but an additional up sweep under changed conditions. The right-hand series of points were measured for increasing field on a crystal that has been in the antiferromagnetic state for about half an hour, the left-hand series for decreasing field and, immediately afterwards, the middle series again for increasing field.

The angular dependence of the field-parallel magnetization measured at constant field in different directions in the xc plane on sample 3 shows maxima of M in the c direction for fields up to about 0.2 T at 1.2 K and for fields up to about 1.0 T at 4.2 K. In larger fields, the maxima are at $\theta = \pm(26 \pm 5)°$ off the c axis at 1.2 K and 4.2 K.

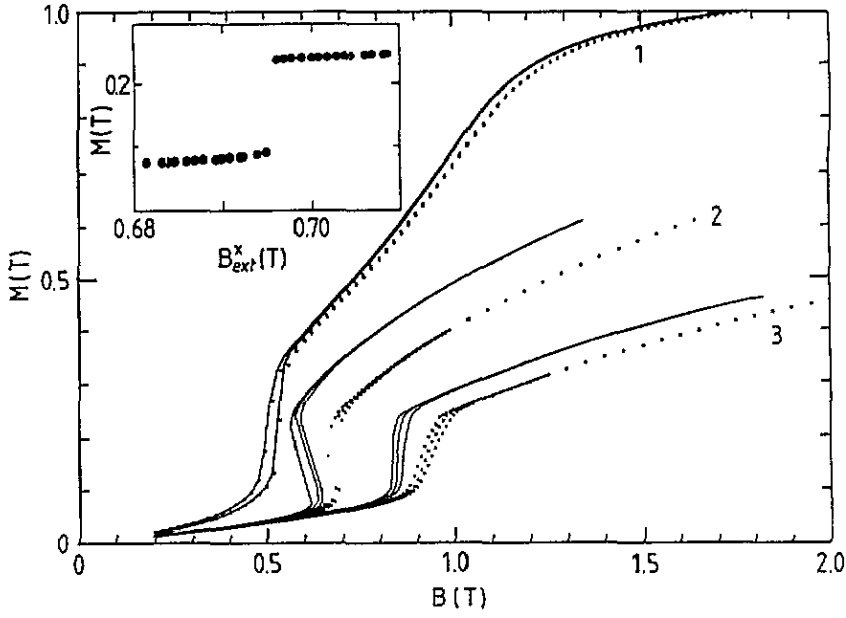

Figure 2. Field dependence of the magnetization for fields along c (curve 1), along x (curve 2) and along a (curve 3), measured on sample 2 at 1.2 K. The dots are the measured points (drawn as a function of the external field B_{ext}), and the full curves represent the values after the demagnetization procedure (drawn as a function of the internal field B_{int}). For details see the text. The inset gives particulars of the points measured in the immediate surroundings of the phase transition for increasing fields along x.

These angles are in excellent agreement with the result of a calculation to determine the crystal-field energy of the individual Tb^{3+} ion in $TbPO_4$ that was performed by Böhm *et al* (1984) using the crystal-field parameters derived from spectroscopic investigations. The single-ion crystal-field energy comes out to show a distinct direction dependence with minima in the (1 1 0) and (1 $\bar{1}$ 0) planes at $\theta = \theta_0$ and $\theta = \pi - \theta_0$ off the c axis with $\theta_0 = 25°$. These eight directions are equivalent as long as the crystal has tetragonal symmetry and does not experience an external or internal magnetic field, which means above $T_{N1} = 2.28$ K. In the classical picture the angular momentum J or magnetic moment μ will lie in one of the eight minima. In a quantum-mechanical description they will tunnel between these minima so that the expectation values are $\langle\mu^x\rangle = \langle\mu^y\rangle = \langle\mu^c\rangle = 0$. In the phase AF with tetragonal symmetry, i.e. for temperatures between T_{N1} and T_{N2}, four of the eight minima will be favoured owing to the magnetic interactions, with the consequence that $\langle\mu^c\rangle \neq 0$. As a result of the monoclinic symmetry in the phase AF' below T_{N2}, two out of the preferred four minima will be even more favoured, leading to either $\langle\mu^x\rangle \neq 0$, $\langle\mu^y\rangle = 0$, $\langle\mu^c\rangle \neq 0$ (domain with distortion in x direction) or $\langle\mu^x\rangle = 0$, $\langle\mu^y\rangle \neq 0$, $\langle\mu^c\rangle \neq 0$ (domain with distortion in y direction). If these ideas were correct for the ordered phases, the magnetic moments of the Tb^{3+} ions, below T_{N2}, should be spacially restricted to a definite plane, which means to the xc or the yc plane for a domain with distortion in x or y direction, respectively. These considerations were the reason for restricting the previous mean-field calculations to two dimensions (Kasten and Üffinger 1985).

3.2. Magnetic susceptibility and domain structure

Measurements of the magnetic susceptibility were mainly undertaken to check the validity of the concept described at the end of the previous section. Thus, the main question was, for a single-domain crystal with distortion in x direction, whether the parallel susceptibility $\chi_{\parallel}$ (static field and AC field along x) and the perpendicular susceptibility $\chi_{\perp}$ (static field along x and AC field along y) will be different or whether $\chi_{\perp}$ will be zero. In the measurements both coil systems were used and for each the sample was fixed in the appropriate orientation. To get the parallel susceptibility $\chi_{\parallel 0}$, the crystal was cooled down without an external field and measured at zero field with the temperature increasing and decreasing in steps of less than 5 mK. Exactly the same curve (apart from a scaling factor) was measured for the perpendicular susceptibility $\chi_{\perp 0}$ of the crystal in the other coil system, again after cooling without an external field and measuring in zero field. This result was to be expected since in both cases the crystal is multi-domain with roughly equal volume parts of domains with distortions in x and y directions. And in both cases, the measured quantity is the sum of the parallel susceptibility of the one domain type and the perpendicular susceptibility of the other domain type. In curve 1 of figure 3, the measured perpendicular susceptibility $\chi_{\perp 0}$ is reproduced instead of the equivalent parallel susceptibility $\chi_{\parallel 0}$ to allow a direct comparison with curve 3 of this figure without need of scaling. The derivative $\mathrm{d}[\chi_{\perp 0}(T)T]/\mathrm{d}T$ (curve 2 of figure 3) shows two maxima corresponding to the transition temperatures T_{N1} and T_{N2}. Next, the crystal in the coil system for measuring the perpendicular susceptibility was premagnetized at 1.5 K in a field of 4 T along x to make it single-domain with distortion in x direction. The field was reduced to 0.1 T to keep the crystal single-domain. Then the perpendicular susceptibility $\chi_{\perp x}$ was measured (see curve 3 of figure 3). There is virtually no difference to the upper curve of $\chi_{\perp 0}$. Additionally, both curves are almost in full agreement (except for the scaling factor) with the susceptibility $\chi_{\parallel a}$, measured in zero field with the AC field along a (lower curve of figure 3), taken from Bluck and Kahle (1988).

Thus it turns out that, for low fields along x, the measured parallel ($\chi_{\parallel 0} \equiv \chi_{\perp 0}$) and perpendicular ($\chi_{\perp x}$) susceptibilities are equal. This can be explained by one of the two following alternatives. (i) The crystal was multi-domain at the measurement of the parallel as well as the perpendicular susceptibility because either the field of 4 T was not sufficient to make the crystal single-domain or the field of 0.1 T was too small to keep it single-domain. (ii) The crystal was really or predominantly single-domain at the measurement of the perpendicular susceptibility; then the consequence is that, referring to the basal plane of the crystal, the parallel and perpendicular susceptibilities of a single-domain crystal are actually equal.

Our studies of the optical birefringence of $TbPO_4$ (see paper III) have clearly shown that a crystal will become single-domain at 1.5 K in a field larger than 0.7 T along x and it will stay really or predominantly single-domain even at zero field. Hence, there is every reason to believe that the second alternative is the correct one. Consequently, the theoretical model, mentioned at the end of section 3.1, will be refined in paper III.

The result that was obtained for the susceptibility can likewise be derived from the study of the magnetization for fields along x (curve 2 of figure 2). At low fields, the same magnitude is measured for increasing as well as for decreasing fields. In the beginning of the cycle, the crystal was multi-domain (cooled in zero field); at the end, however, it was single-domain (premagnetized in a field of 1.6 T). Hence, it follows

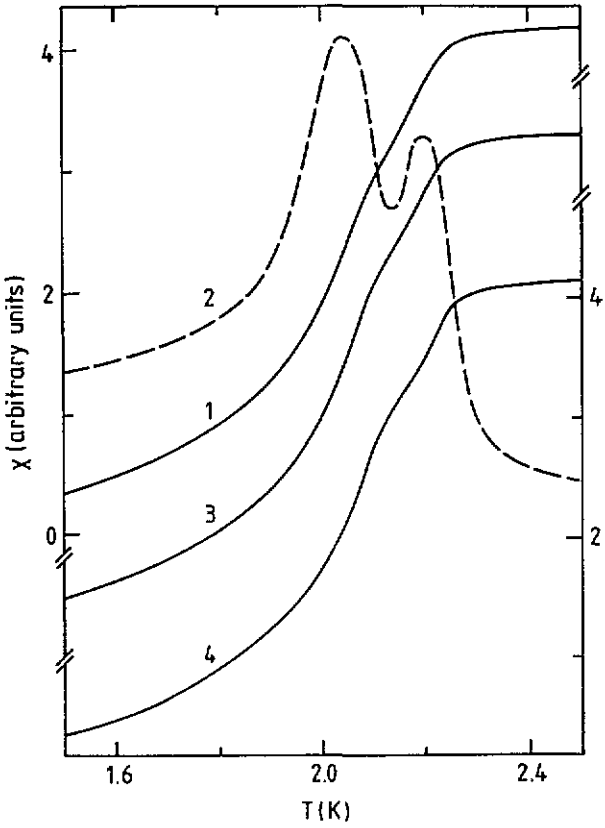

Figure 3. Temperature dependence of the susceptibility. Curve 1: $\chi_{\perp 0}$ measured on sample 2 at zero static field; the crystal was multi-domain. Curve 2: derivative $d(\chi_{\perp 0}T)/dT$ of curve 1. Curve 3: $\chi_{\perp x}$ measured on sample 2 at $B_{ext}^{x} = 0.1$ T with the AC field along y; the crystal was supposed to be almost single-domain with distortion in x direction. Curve 4: $\chi_{\parallel a}$ measured on a crystal of dimensions $a \times b \times c = 1.25 \times 1.25 \times 3.5$ mm^3 at $B_{ext}^{a} = 0.1$ T with the AC field along a, scaled to curves 1 and 3, taken from Bluck and Kahle (1988). In all cases, the averaged susceptibility curves measured for decreasing temperature are reproduced with an arbitrary offset.

that for low fields the magnetization along x for domains with distortion in x and y directions must be equal.

To support the findings on the domain structure, we have tried to observe the domains in a $TbPO_4$ crystal with an arrangement developed by Klein *et al* (1972) and Leask *et al* (1973). Sample 4 was mounted between crossed polaroids (polarization direction along a or b, respectively) and cooled down to 1.4 K. A variable magnetic field could be applied along x. The sample was illuminated along c with parallel white light. Its image showed no structure at all and no dark lines as indications of domain walls, it was just a lightly coloured area, which became a bit brighter at fields above 0.7 T. Rotation of the sample relative to the polaroids did not change the image noticeably. The reason for not being able to observe the domains or domain walls will be the fact that the birefringence is very small ($\delta n_{yx} \simeq +25 \times 10^{-6}$ in the blue and

$\simeq -25 \times 10^{-6}$ in the red region of the spectrum and a zero passage in between; see paper III). Additionally the domains may be thinner than the crystal in the direction of the light path, thus partially cancelling the effect of birefringence. Hence, in this way it is not possible to decide whether the crystal is single- or multi-domain.

3.3. Phase diagram

The curves measured and described in the previous sections were used to determine the phase diagram of $TbPO_4$ for the three field directions along c, x and a. The inflection points above the maximum of the respective derivatives $dM(T)/dT$, $dM(B)/dB$ or $d[\chi(T)T]/dT$ were regarded as the phase transitions. These points are inserted in the phase diagram of figures 5 and 7 of paper III. A comparison with the results of former publications shows excellent agreement. All phases are confirmed. However, none of the phase transitions that additionally were observed in the birefringence measurements of paper III could be discovered. A detailed discussion will be given in paper III in connection with the results of an improved theoretical treatment.

4. Conclusions

This renewed and expanded investigation on the magnetic properties of $TbPO_4$ has above all yielded one important and unexpected result. In the antiferromagnetic phase AF′ with monoclinic symmetry, i.e. below $T_{N2} = 2.13$ K, the parallel and perpendicular susceptibilities, measured with the AC field along x and y on a single-domain crystal with distortion in x direction, are equal. This result signifies that the model developed by Kasten and Üffinger (1985) to describe the low-temperature properties of $TbPO_4$ in mean-field theory has to be extended accordingly. Obviously, it is not justified to restrict the effectiveness of the interactions to the monoclinic plane (xc or yc plane, respectively). One has to include the interactions in the perpendicular direction (y or x direction, respectively), to be able to reproduce the behaviour of the Tb^{3+} moments in all three dimensions. In paper III the theoretical basis will be widened correspondingly. With this, the equality of the parallel and perpendicular susceptibilities will be verified.

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