Magnetic and thermal properties of the two-level magnetic system, $KTm(MoO_4)_2$

2002 J. Phys.: Condens. Matter 14 9693

(http://iopscience.iop.org/0953-8984/14/41/324)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 9693–9703 PII: S0953-8984(02)34488-6

Magnetic and thermal properties of the two-level magnetic system, $KTm(MoO_4)_2$

V A Pashchenko[1,6], V G Borisenko[2], E N Khats'ko[1], A S Cherny[1], C Paulsen[3], A Feher[4], M Orendáč[4], A Orendáčová[4], A G M Jansen[5] and P Wyder[5]

[1] B Verkin Institute for Low Temperature Physics and Engineering, NASU, 61103 Kharkov, Ukraine
[2] Department of Physics, Kharkov Air Force Institute, 61064 Kharkov, Ukraine
[3] Centre de Recherches sur les Très Basses Températures, CNRS, BP 166, 38042 Grenoble Cedex 9, France
[4] Department of Experimental Physics, P J Šafárik University, Park Angelinum 9, 04154 Košice, Slovakia
[5] Grenoble High Magnetic Field Laboratory, MPI-FKF and CNRS, BP 166, 38042 Grenoble Cedex 9, France

E-mail: pashchenko@physik.uni-frankfurt.de

Received 4 March 2002, in final form 8 August 2002
Published 4 October 2002
Online at stacks.iop.org/JPhysCM/14/9693

Abstract

The magnetic susceptibility and specific heat of single crystals of $KTm(MoO_4)_2$ in the temperature interval 0.1–300 K are investigated. It is shown that the ground state of the rare-earth magnetic system of the Tm^{3+} ions can be represented by two close-lying singlet levels (a non-Kramers quasidoublet with $M_J = |\pm 6\rangle$) separated by a rather large energy interval from the excited levels. The effect of the 'freezing' of energy levels on magnetic susceptibility and the Schottky anomaly on magnetic specific heat have been observed in the low-temperature region $T < 2.5$ K. These results show that this magnetic system can be considered as a simple two-level quantum system over a wide temperature range.

1. Introduction

The potassium thulium molybdate $KTm(MoO_4)_2$ has a layered crystal structure with orthorhombic symmetry in the space group $Pbcn$ (D_{2h}^{14}) [1]. This compound is ideally suited to the study of high-symmetry effects of crystal-field interactions, which are so important for understanding various electronic properties and developing rare-earth devices. As is well known, for a crystal field of symmetry D_{2h}^{14}, the degeneracy of the ground term $^3H_6$ of the Tm^{3+}

[6] Author to whom any correspondence should be addressed.

ion ($S = 1$, $L = 5$, $J = 6$) should be removed completely by a ligand field leading to a set of 13 singlets. However, in the case of $KTm(MoO_4)_2$, the nearest high-symmetry environment plays a prevailing role in the splitting of the multiplet $^3H_6$ caused by the action of the crystal field on the rare-earth ion. The nearest oxygen environment of the rare-earth ion is a slightly distorted square antiprism TmO_8, having a higher symmetry D_{4d}. According to Harris [2], the crystal-field interaction here is dominated by terms with axial symmetry about the z axis (C_2^0, C_4^0 and C_6^0) and the $^3H_6$ term of the non-Kramers ion Tm^{3+} should be split into a set of six doublets characterized by $M_J = |\pm 6\rangle, |\pm 5\rangle, |\pm 4\rangle, |\pm 3\rangle, |\pm 2\rangle, |\pm 1\rangle$ and a singlet $|0\rangle$. The typical energy scale of the crystal-field Stark splitting of the ground term $^3H_6$ of the Tm^{3+} ion in a crystal can achieve a few hundred cm^{-1} [2]. The distortion of the square antiprism TmO_8 and the next nearest environment give small corrections of lower symmetry in the crystal-field environment of the Tm^{3+} ion. The small influence of these low-symmetry components of the crystal field is responsible for a weak splitting of the doublets. Thus, the lowest pair of nearly degenerate energy levels is separated by a large energy interval from the next higher group of Stark levels of the $^3H_6$ multiplet and completely determines the magnetic and thermal properties of $KTm(MoO_4)_2$ over a wide temperature range.

Recent ESR measurements [3] of low-energy electronic levels in a single crystal of $KTm(MoO_4)_2$ have established that the ground state of the Tm^{3+} ions is a non-Kramers doublet consisting mainly of $M_J = |\pm 6\rangle$ with relatively small zero-field splitting $\Delta/k = 2.33$ cm^{-1} and a single g value of 13.99. Optical experiments [4] have shown that the nearest Stark level of the trivalent Tm is located about 200 cm^{-1} higher than the ground doublet. Therefore, this compound can be considered to be an almost ideal quantum two-level object with a very large projection of magnetic moment on each of the two levels. The study of the features of the behaviour of such magnetic systems at low temperatures is of special interest, because the occurrence of magnetic ordering in the absence of a magnetic field depends on the relation between the energy of exchange and/or dipole–dipole interactions and the energy splitting of the quasidoublet.

Here, we present magnetic susceptibility and specific heat measurements made on single crystals of $KTm(MoO_4)_2$ in order to determine the influence of low-symmetry crystal-field interactions on the magnetic and thermodynamic properties of rare-earth magnetic materials.

2. Experimental technique

High-quality single crystals of $KTm(MoO_4)_2$ were obtained by means of a flux growth method [5]. The structure consists of infinite chains of octacoordinated TmO_8 polyhedra elongated along the c axis and connected at their edges. The magnetic susceptibility was measured by the Faraday method on a magnetic balance with autocompensation in a magnetic field $H = 0.3$ T. These measurements were carried out in the temperature range 2–300 K for three crystallographic directions of the crystal. At lower temperatures magnetic measurements ($H \parallel c$) were made using three different techniques. In the temperature range 0.075–2 K, the measurements of $\chi_{dc}(T)$ were performed on a SQUID magnetometer developed at the CRTBT (Grenoble). The magnetometer is equipped with a miniature dilution refrigerator which allows measurements to be read down to 75 mK and in fields up to 8 T. In the temperature range 0.1–3 K the $\chi_{ac}(T)$ data were obtained using a SQUID magnetometer at a frequency of 0.11 Hz and a field of less than 10^{-5} T. In the temperature range 0.5–2 K, the $\chi_{ac}(T)$ was measured by an induction technique using a mutual induction bridge at 30 Hz in zero field. All three techniques show a good agreement in the obtained experimental data.

The dimensions of the single-crystal sample used for specific heat measurements were $8 \times 13 \times 1$ mm^3 with a weight of 352 mg. The specific heat measurements were performed

in the temperature range from 100 mK up to 2.5 K using a dual-slope method [6]: a relaxation technique established in a commercial TLE 200 ^{3}He–^{4}He dilution refrigerator made by Oxford Instruments. The temperature of the sample was monitored by a RuO_2 resistance thermometer manufactured by Dale Electronics with a nominal value of 4.7 kΩ, calibrated against a commercial germanium thermometer Lake Shore GR 200 A-30. The thermometer was varnished directly onto the sample with GE 7031 varnish. For homogeneous heating of the sample, a manganin wire with diameter of 50 μm formed into meanders was used, varnished onto the opposite side of the crystal. The experimental data were corrected for addenda which for practically the whole temperature region did not exceed an experimental inaccuracy of 5%.

3. Magnetic susceptibility

The results of the magnetic susceptibility measurements on a single crystal of $KTm(MoO_4)_2$ are shown in figures 2–4. The obtained experimental data show a strong anisotropy of magnetic properties of this compound. In the directions perpendicular to the direction of magnetic moment μ, the rare-earth non-Kramers ions with quasidoublet ground state are not magnetized in a linear field approach (see the formula (1), for example). Due to this fact and the strong anisotropy of the g factor (for Tm^{3+} in $KTm(MoO_4)_2$: $g_{z'} = 13.99$, $g_{x'} = g_{y'} = 0$ [3]), these kinds of ions are usually called 'Ising ions', emphasizing the analogy between the behaviour in a magnetic field of the moments for these ions and for spins in the Ising model. Here we shall not analyse the magnetic susceptibility along the a and the b axes. For these directions, the susceptibilities have a complex magnetic behaviour (see the inset in figure 2). Moreover, the obtained experimental values result from the two parts coming from the two non-equivalent centres ($\theta = \pm 7.6°$ [3]) and strongly depend upon the accuracy of external field orientation. Within a two-level quantum system with two non-equivalent centres, the rough estimation of the total magnetization along crystallographic directions using formula (1) gives the following ratio of the amplitudes: M_{c-axis}:$M_{a-axis} = 0.983$:0.018. As can be seen in figure 2, at low temperature we have obtained the same ratio in our experiments. Thus, the low-temperature increase in magnetic susceptibility does not indicate the presence of an impurity in our sample. It is due to the projections of magnetic moments of a two-level system with two different centres on the applied field. That we obtain the pure perpendicular component of magnetic susceptibility of one magnetic centre is baffling. It should be noted that $\chi_a(T)$ and $\chi_b(T)$ show a very broad maximum around 200 and 160 K, respectively.

For an external magnetic field orientated along the c axis, magnetic susceptibility increases sharply with decrease in temperature. It should be noted that this temperature dependence does not have a Curie-like behaviour. In figures 2 and 3, the calculated curve using the formula $\chi_0(T) = J(J+1)g_J^2\mu_B^2/3kT$ is shown in order to stress a significant difference between the magnetic behaviour of the thulium system in $KTm(MoO_4)_2$ and the prediction of the Curie law for an ion with $J = 6$ and $g_J = 7/6$. As can be seen in figure 3, the magnetic properties of $KTm(MoO_4)_2$ are mainly determined by the crystal-field interactions and the Curie–Weiss approach requires much higher temperature measurements.

Below we shall discuss the obtained experimental data for two temperature intervals.

3.1. Magnetic susceptibility in the temperature interval 2–300 K

The results of resonant measurements [3] show that the ground state of the Tm^{3+} ions in a single crystal of $KTm(MoO_4)_2$ is a quasidoublet with the maximum possible M_J value, which is separated from the excited levels by a rather large energy interval [4]. However, in the high-temperature region, an influence of thermal population of the excited levels of the

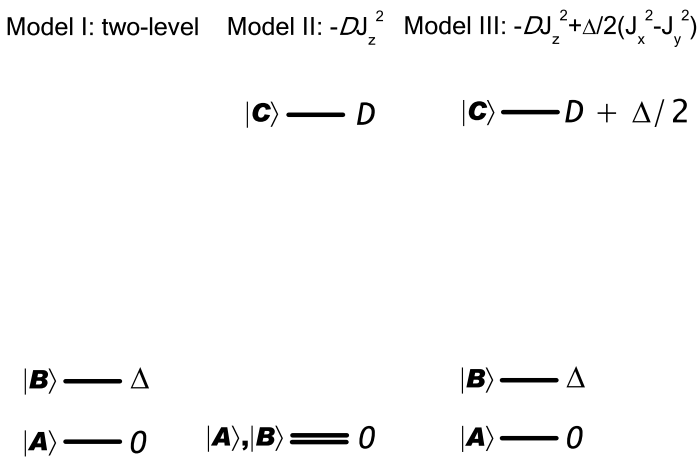

Figure 1. Schematic structure of electronic levels of the Tm^{3+} ion for the three models of crystal field. The states $|A\rangle$ and $|B\rangle$ are characterized by M_J equal to -6 and $+6$ respectively.

multiplet $^3H_6$ on the behaviour of magnetic susceptibility is expected. A precise determination of energy level structure of the Tm^{3+} ion in $KTm(MoO_4)_2$ would involve the diagonalization of the Hamiltonian consisting of 13 free ion parameters including the spin–orbit constant and the crystal-field parameters in the complete basis of the $4f^{12}$ configuration. However, up to now, the exact structure of electronic levels of the lowest multiplet $^3H_6$ for the Tm^{3+} ions in $KTm(MoO_4)_2$ has not been restored. Therefore, for the description of the magnetic and thermal properties of the compound $KTm(MoO_4)_2$ it is possible to use an incomplete Hamiltonian for the crystal field using an 'effective' Hamiltonian constructed on the basis of the wavefunctions of only certain Stark levels of the split multiplet $^3H_6$. This approach is justified in that temperature region in which only the chosen electronic levels of the Tm^{3+} ion are populated, and in that range of magnetic fields where the magnetic splitting is much smaller than the energy interval between the ground and the excited levels. Therefore, for the estimation of the contribution from the excited electronic levels of the Tm^{3+} ion to the temperature dependence of magnetic susceptibility of $KTm(MoO_4)_2$ in the temperature interval $2\ \mathrm{K} < T < 300\ \mathrm{K}$ (see figures 2 and 3) we used the following three 'effective' models:

(a) *model I*: a quantum two-level system with $M_J = |\pm 6\rangle$, which does not take into account the presence of the excited levels;
(b) *model II*: a three-level system, in which the lowest quasidoublet is not split, but the excited singlet is included;
(c) *model III*: in which both the lowest split quasidoublet, and the first excited singlet are considered (see figure 1).

As will be clear from the subsequent analysis, in view of the greater number of the excited levels it would not be expedient to use more complex models for the explanation of our experimental data.

There now follows a brief review of the analysis of the three models.

Model I: a quantum two-level system. When the quasidoublet is a ground state of the non-Kramers ion Tm^{3+} separated by a rather large energy interval from the excited levels, the magnetization of the rare-earth subsystem for an external magnetic field along the c axis can

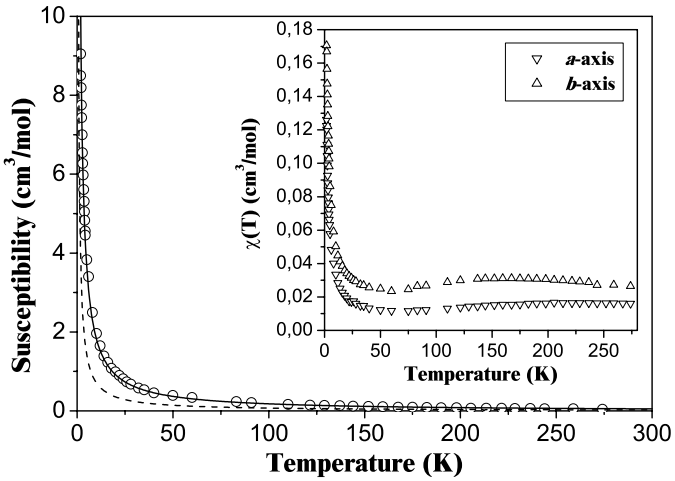

Figure 2. Magnetic susceptibility of the rare-earth subsystem of the Tm^{3+} ions with the external magnetic field along the c axis in the temperature interval 2 K $< T <$ 300 K. The solid curve represents the results of calculations using the formulas (1), (4) and (6). The dashed curve is the Curie law $\chi_0(T) = J(J+1)g_J^2\mu_B^2/3kT$ with $J = 6$ and $g_J = 7/6$. The inset shows the obtained experimental data for the a and the b crystallographic directions.

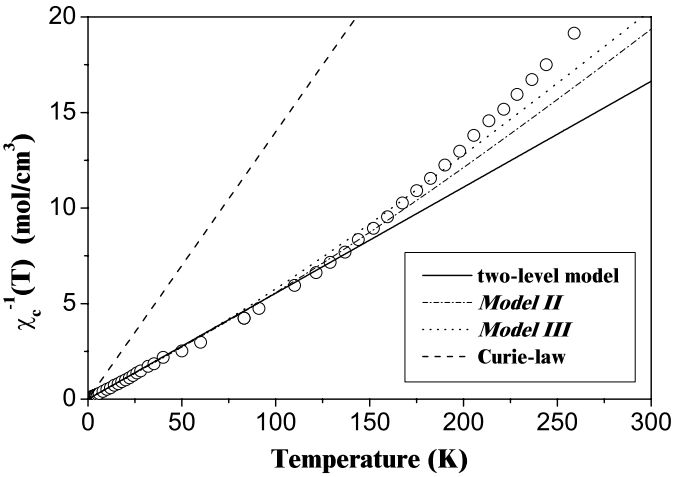

Figure 3. Temperature dependence of the inverse magnetic susceptibility $\chi_c^{-1}(T)$ in $KTm(MoO_4)_2$. The solid, dash–dotted and dotted curves are the susceptibility of two-level quantum magnet with $M_J = |\pm 6\rangle$, the susceptibility within the framework of the model $\mathcal{H}_{cf} = -DJ_z^2$ and $\mathcal{H}_{cf} = -DJ_z^2 + \frac{\Delta}{2}(J_x^2 - J_y^2)$, respectively. The dashed line is the Curie law $\chi_0(T) = J(J+1)g_J^2\mu_B^2/3kT$.

be described by a simple two-level model over a wide temperature interval. For a two-level quantum system with the projections of magnetic moments at the upper state $-\mu = g_J\mu_B J$ and at the lower state $\mu = g_J\mu_B J$ along the field direction the magnetization becomes:

$$M(H,T) = g_J\mu_B J\cos\theta\tanh\left(\frac{g_J\mu_B J\cos\theta H}{kT}\right). \tag{1}$$

This model is completely coincident with a conventional model for an effective spin $S = 1/2$ and $g_{z'} = 2Jg_J = 14$ considered in [3]. In this expression, $M(H, T)$ is the magnetization (in the calculation for one Tm^{3+} ion) in the direction of the magnetic field along the c axis; θ is the angle between the magnetic field and the direction of local z' axes for two non-equivalent centres ($\theta = \pm 7.6^\circ$ with respect to the c axis [3]). It should be noted that the presence of two non-equivalent centres of the Tm^{3+} ions does not have a significant influence on the magnetization along the c axis due to the small value of θ and the symmetric position of the local z' axes with respect to the c axis. Thus, for the direction of the magnetic field along the c axis, it is possible without loss of a generality to use the 'one-centre' description for the magnetic structure of $KTm(MoO_4)_2$. Without any fit parameters, by using only the value of angle θ from [3], the magnetic susceptibility $\chi_c(T)$ calculated on the basis of expression (1) is in excellent agreement with the experimental data below 150 K (see solid curves in figures 2 and 3).

Model II: a crystal field of the elementary form $\mathcal{H}_{cf} = -DJ_z^2$ ($D > 0$). At the first step of approximation, which reflects the axial symmetry of the crystal-field interactions, we can use the Hamiltonian with *a crystal field of the elementary form* $\mathcal{H}_{cf} = -DJ_z^2$. In this case with the crystal field part in the Hamiltonian $\mathcal{H}_{cf} = -DJ_z^2$, the sign of the constant D will determine the type of anisotropy of the paramagnetic phase: for $D < 0$ 'easy plane' (xy plane) and for $D > 0$ 'easy axis' (z axis). Here we can take advantage of earlier results for an ion with $J = 1$ in the crystal field of the simple form $\mathcal{H}_{cf} = -DJ_z^2$ [7, 8]. The energy spectrum and the wavefunctions of the ion with $J = 1$ in the crystal field $\mathcal{H}_{cf} = -DJ_z^2$ will be equal:

$$\begin{aligned} &E_0 = 0, \qquad \psi_0 = |J = 1, M_J = 0\rangle \\ &E_{\pm 1} = -D, \qquad \psi_{\pm 1} = |J = 1, M_J = \pm 1\rangle. \end{aligned} \tag{2}$$

Thus, within the framework of this model for a magnet with an 'easy axis' anisotropy $D > 0$, the lowest doublet is not split ($\Delta = 0$), and the value $|D|$ defines an energy interval up to a next higher singlet state (see schematic structure of the levels in figure 1). The components of magnetic susceptibility of such a system are:

$$\begin{aligned} \chi_{zz}(T) &= \frac{2g_J^2\mu_B^2}{kT[2 + \exp(-D/kT)]} \\ \chi_{\perp}(T) &= \frac{2g_J^2\mu_B^2[1 - \exp(-D/kT)]}{D[2 + \exp(-D/kT)]}. \end{aligned} \tag{3}$$

At high temperatures $T \gg D/k$, the susceptibility of such a paramagnet is isotropic: $\chi_{zz}, \chi_{\perp} \to 2g_J^2\mu_B^2/3kT$. With decreasing temperature for the case $D > 0$ the magnetic susceptibility along the easy axis grows as $1/T$ and at $T \ll D/k$ corresponds to the susceptibility of the two-level system. Thus along the direction perpendicular to the easy axis, the magnetic susceptibility has a Van Vleck origin and is due to the mixing of the excited states with the ground state. With decreasing temperature this susceptibility tends to a constant value $\chi_{\perp} \to g_J^2\mu_B^2/D$.

For the axial symmetry crystal field $\mathcal{H}_{cf} = -DJ_z^2$ (we consider the parameter $D > 0$) the behaviour of magnetic system at $J > 1$ does not differ qualitatively from the case for $J = 1$ [8]. Therefore, it is enough only to renormalize the value of the magnetic moment $g_J\mu_B \to Jg_J\mu_B$. Thus the temperature dependence of the magnetic susceptibility of the Tm^{3+} ions with external magnetic field along the c axis is given by:

$$\chi_{zz}(T) = \frac{2J^2g_J^2\mu_B^2}{kT[2 + \exp(-D/kT)]}. \tag{4}$$

Using the value of $D/k = 200$ K [4], the result of calculation for $\chi_{zz}(T)$ using the expression (4) as well as for a two-level system are in good agreement with the experimental data presented in figure 2.

Model III: a crystal field of the form $\mathcal{H}_{cf} = -DJ_z^2 + \frac{\Delta}{2}(J_x^2 - J_y^2)$ $(D > 0, \Delta > 0)$. This model takes into account the presence of the finite splitting of the lowest quasidoublet under the action of the low-symmetry part of the crystal field, and the next higher excited singlet. If the readout of the energy is made from the lowest level of the rare-earth ion, the energy spectrum of the Tm^{3+} ion has the following form:

$$E_{|A\rangle} = 0; \qquad E_{|B\rangle} = \Delta; \qquad E_{|C\rangle} = D + \frac{\Delta}{2} \tag{5}$$

and is represented schematically in figure 1. Obviously, at $\Delta \ll D$ and/or at $\Delta \to 0$ the results for this model coincide with the results for the previous model ($\mathcal{H}_{cf} = -DJ_z^2$). At the finite splitting Δ of the ground state, the temperature dependence of magnetic susceptibility of the Tm^{3+} ions with external magnetic field along the c axis can be described by the following expression:

$$\chi_{zz}(T) = \frac{J^2 g_J^2 \mu_B^2 \left[1 + \exp\left(-\frac{\Delta}{kT}\right)\right]}{\frac{\Delta}{2}\left[1 + \exp\left(-\frac{\Delta}{kT}\right) + \exp\left(-\frac{D+\frac{\Delta}{2}}{kT}\right)\right]}, \tag{6}$$

where $g_J = 7/6$, $J = 6$. For *model III* the best fit parameters are $D/k = 200$ K and $\Delta/k = 3.5 \pm 0.1$ K.

All the above-mentioned models describe the experimental data in figure 2 with the same degree of the accuracy (the value of deviation does not exceed the thickness of a solid line). The difference between *models I, II* and *III* can be seen in the temperature dependence of the inverse magnetic susceptibility presented in figure 3. The three-level system describes more clearly the high-temperature part of the magnetic susceptibility of $KTm(MoO_4)_2$.

Within the framework of *model II* the estimation of the perpendicular component is $\chi_\perp(T \to 0) \approx N_A J^2 g_J^2 \mu_B^2 / D \approx 0.088$ cm^3 mol^{-1}, which to an order of magnitude coincides with observable maxima of $\chi(T)$ along the a and b axes (0.015 and 0.031 cm^3 mol^{-1}). As is shown in figure 3, at the temperatures below 150 K the magnetic behaviour of the rare-earth subsystem of the Tm^{3+} ions in single crystal $KTm(MoO_4)_2$ is well described by the two-level quantum system. Thus we can conclude that the influence from the excited next higher group of Stark levels into multiplet $^3H_6$, split by a crystal field, is negligibly small in this temperature range.

3.2. Magnetic susceptibility of the two-level quantum system at low temperatures $T < 2$ K

The above results suggest that at low temperatures the temperature dependence of magnetic susceptibility may be well described by a quantum two-level model. However, at low temperatures it may be necessary to take into account the influence of exchange and/or dipole–dipole interactions, which for a certain ratio between the splitting Δ of the quasidoublet and the constant of the exchange interaction λ can result in short-range or perhaps even long-range magnetic order in a magnetic system. According to [8, 9], at finite temperatures the behaviour of magnetic susceptibility of a two-level quantum system in the 'pre-critical state', when the parameter $Q = \mu^2\lambda/(\Delta/2) < 1$ (λ is the constant of exchange interaction), may be described by the following expression:

$$\chi_{zz}(T) = \frac{\mu^2}{\frac{\Delta}{2}\left[\tanh^{-1}\left(\frac{\Delta}{2}/kT\right) - Q\right]}. \tag{7}$$

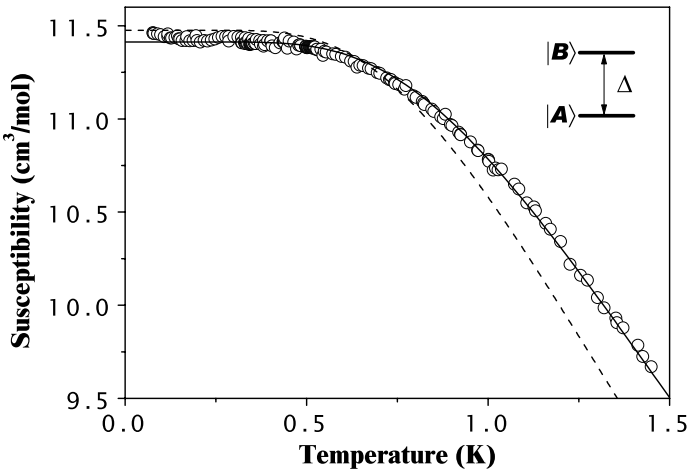

Figure 4. Magnetic susceptibility of a single crystal of $KTm(MoO_4)_2$ with the external magnetic field along the c axis in the temperature interval 0.076–1.5 K ($H = 962$ Oe). The solid curve is the result of the calculation using formula (7) with the following parameters: $\Delta/k = 3.49$ K; $Q = -0.08$; the dashed curve is the best fit for model III (6) with the parameters: $D/k = 200$ K, $\Delta/k = 3.20$ K. The inset schematically shows the energy structure of the quantum two-level system.

In this expression, $\mu = g_J\mu_B|\langle A|J_z|B\rangle|$ is the magnetic moment of a quantum two-level system with states $|A\rangle$ and $|B\rangle$, Δ is the energy interval between these levels (see inset in figure 4), and the value Q characterizes the relation of the energy of exchange (or dipole–dipole) interaction in comparison with the crystal field. The susceptibility $\chi_{zz}(T)$ at $T \to 0$, which in this case is connected to the population of these levels with states $|A\rangle$ and $|B\rangle$, tends to lie at a constant value. So at $Q = 1$ the saturation of magnetic susceptibility at $T \to 0$ will occur at a level of $\mu^2/(\Delta/2)$.

The result of the calculation using formula (7) with the parameters $\Delta/k = 3.49 \pm 0.05$ K, $Q = -0.08$ is shown in figure 4 as a solid curve. As can be seen in figure 4, at low temperatures the model (7) well describes the magnetic susceptibility of $KTm(MoO_4)_2$ when the external magnetic field is along the c axis. The small value of the parameter Q indicates that the value of the exchange or dipole–dipole interactions is small in comparison with the crystal field. This allows us to interpret the plateau in the low-temperature magnetic susceptibility data as being due to the 'freezing' of magnetic states into the two-level quantum system. The value obtained for the splitting of the non-Kramers doublet $\Delta/k = 3.49$ K in $KTm(MoO_4)_2$ is close to that obtained from resonant measurements [3]. So, from the estimation of the work [3], the value of the splitting of the quasidoublet in a zero magnetic field is 2.33 cm^{-1}, which corresponds to 3.35 K.

4. Specific heat

The low-symmetry crystal field lifts the degeneracy of the ground term $^3H_6$ of the Tm^{3+} ion into $(2J + 1)$ Stark components and the thermal population of these states gives rise to a Schottky anomaly in the specific heat of a crystal:

$$C_S(T) = R\frac{\partial}{\partial T}\left[\frac{\sum_{i=1}^{2J+1} E_i g_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_{i=1}^{2J+1} g_i \exp\left(-\frac{E_i}{kT}\right)}\right], \tag{8}$$

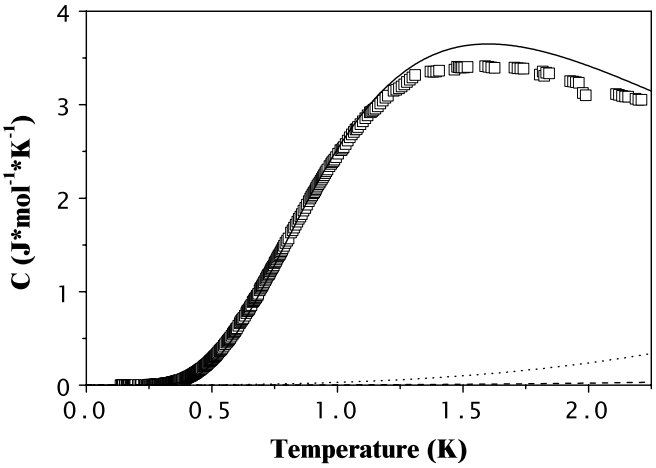

Figure 5. Temperature dependence of the specific heat of a single crystal of $KTm(MoO_4)_2$ in the temperature interval of 0.130–2.2 K. The solid curve is the calculated curve for two different models (10) and (12). The dotted curve is the upper limit of the possible lattice contribution (9). The dashed curve is the low-temperature extrapolation of the specific heat of the isomorphous diamagnetic compound $KLu(MoO_4)_2$ [10].

where $R = N_A k$, g_i denotes the degree of degeneracy, E_i is the energy of the ith level and $(2J + 1)$ is the total number of Stark components in the ground term. The small crystal-field splitting of the ground quasidoublet for $KTm(MoO_4)_2$ gives rise to a peak at low temperatures, and due to the fact that the next Stark levels are well separated from quasidoublet, the contribution of the other excited levels can be neglected in the following calculations.

The results of the specific heat measurements at low temperatures on a single crystal of $KTm(MoO_4)_2$ are shown in figure 5. The obtained experimental data are a sum of two parts: the Schottky anomaly and the lattice contribution. The lattice contribution to the specific heat of $KTm(MoO_4)_2$ in the measured temperature region is negligible. For example, the low-temperature extrapolation of the specific heat of the isomorphous diamagnetic compound $KLu(MoO_4)_2$ [10] does not exceed our experimental accuracy (see the dashed curve in figure 5). Nevertheless, in order to estimate an upper bound to possible correction we used the results of low-frequency phonon spectra measurements made on the isomorphous compounds $KRe(MoO_4)_2$, where Re = Y, Er, Dy [11]. Although these compounds showed some slight anisotropy in their phonon spectrum, we have estimated the Debye temperature θ_D by using the average value of the energy of three 'acoustic' phonon modes for three crystallographic directions. We find an average value of $\theta_D \approx 40.3$ K, which for the low-temperature region $\hbar\omega/kT \gg 1$ allows us to approximate the lattice contribution as:

$$C_L(T) = 234R\left(\frac{T}{\theta_D}\right)^3. \tag{9}$$

For our temperature interval this contribution is also negligibly small in comparison to the magnetic contribution (see the dotted curve in figure 5).

We have analysed our data with respect to the three previously mentioned models:

Model I. The expression for the specific heat of a two-level system with the splitting of Δ is well known:

$$C(T) = R\left(\frac{\Delta}{kT}\right)^2 \frac{\exp\left(\frac{\Delta}{kT}\right)}{\left[1 + \exp\left(\frac{\Delta}{kT}\right)\right]^2}. \tag{10}$$

This expression has only one fitting parameter, Δ/k. This should be compared with magnetic susceptibility measurements for the same model where two fitting parameters were necessary (the g factor and the splitting Δ/k in a zero field). The best agreement with the experimental data in the frame of this model was found using $\Delta/k = 3.84 \pm 0.05$ K (see the solid curve in figure 5).

Model II. The next simplest approximation we consider is a non-split lowest doublet (i.e. the splitting is negligibly small) and one excited singlet. There is also one parameter D—the energy interval between the non-split doublet and next singlet. The dependence of a specific heat on the temperature in this case is given by the expression

$$C(T) = 2R\left(\frac{D}{kT}\right)^2 \frac{\exp\left(\frac{D}{kT}\right)}{\left[1 + 2\exp\left(\frac{D}{kT}\right)\right]^2}, \tag{11}$$

which has a maximum of $C(T)$ situated at approximately $T_{max} \approx 0.45D/k$. Using the value of $D/k = 200$ K, this would imply a maximum in $C(T)$ at $T_{max} \sim 90$ K, which obviously contradicts our measured specific heat data. Such a value of T_{max} is caused by the fact that for this model the main contribution to a Schottky anomaly is given by the next higher excited singlet. Conversely, by using a small parameter D/k (D/k is of the order of Δ/k) we can obtain a similar peak at the same temperature as in our experiment, but the amplitude of the maximum $C_{max}(T_{max})$ for such three-level systems is much smaller then the obtained experimental data.

Model III. The temperature dependence of the magnetic part of the specific heat for a split lowest doublet and one excited singlet has the following form:

$$C(T) = R\left(\frac{1}{kT}\right)^2 \frac{\Delta^2 \exp\left(-\frac{\Delta}{kT}\right) + \left(D + \frac{\Delta}{2}\right)^2 \exp\left(-\frac{D+\frac{\Delta}{2}}{kT}\right) + \left(D - \frac{\Delta}{2}\right)^2 \exp\left(-\frac{D+\frac{3\Delta}{2}}{kT}\right)}{\left[1 + \exp\left(-\frac{\Delta}{kT}\right) + \exp\left(-\frac{D+\frac{\Delta}{2}}{kT}\right)\right]^2}, \tag{12}$$

where there are two parameters, D/k and Δ/k. It should be noted that the variation of the parameter D/k has little effect on the shape of the curve, which is more sensitive to change in the parameter Δ/k. The best agreement with experimental data is found for the following parameters: $D/k = 200$ K, $\Delta/k = 3.84 \pm 0.05$ K (this curve in figure 5 coincides perfectly with the curve for a two-level system in model I). Thus, taking into account the next higher excited singlet state situated above the ground quasidoublet, there is no influence on the temperature dependence of specific heat $C(T)$ at low temperatures. Thus we conclude that the character of the Schottky anomaly in the low-temperature region is determined mainly by the lowest quasidoublet.

The small discrepancy between the experimental data and calculated curve near the maximum of specific heat is caused, apparently, either by the real two-centre magnetic structure of the Tm^{3+} ions or by small spin–spin correlations arising at low temperatures.

5. Conclusions

The magnetic susceptibility and the specific heat of the Tm^{3+} ions in a single crystal of $KTm(MoO_4)_2$ have been analysed in the framework of three simple models. These three models give qualitatively similar results, which would explain the magnetic and thermal properties of $KTm(MoO_4)_2$ over a wide range of temperatures. It is shown that the studied magnetic system below $T < 150$ K can be well described as a quantum two-level system consisting mainly of $M_J = |\pm J\rangle$. In the low-temperature region $T < 2.5$ K, in the two-level quantum system the effects of the 'freezing' of energy levels on magnetic susceptibility

and the Schottky anomaly on magnetic specific heat are observed. The value obtained for the zero-field splitting Δ of the two lowest crystalline Stark levels in $KTm(MoO_4)_2$ from magnetic and specific heat measurements is in good agreement with that obtained from resonant measurements. The magnetic susceptibility at low temperatures shows that the influence of exchange or/and dipole–dipole interactions is still small compared with the crystal field effects.

References

[1] Spitsin V I and Trunov V K 1969 *Dokl. Akad. Nauk* **185** 854
[2] Harris E A and Furniss D 1991 *J. Phys.: Condens. Matter* **3** 1889
[3] Pashchenko V A, Jansen A G M, Kobets M I, Khats'ko E N and Wyder P 2000 *Phys. Rev.* B **62** 1197
[4] Kobets M I, Kurnosov V V, Pashchenko V A and Khats'ko E N 1999 *Sov. J. Low Temp. Phys.* **25** 379
[5] Evdokimov A A, Efremov V A, Trunov V K, Kleiman I A and Dsurinsky B F 1991 *Compounds of Rare-Earth Elements. Molybdates. Tungstates* (Moscow: Nauka)
Pelikh L N, Gurskas A A and Zvyagin A I 1980 *Sov. Phys.–Solid State* **22** 155
[6] Riegel S and Weber G 1986 *J. Phys. E: Sci. Instrum.* **19** 790
[7] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
[8] Zvezdin A K, Matveev V M, Mukhin A A and Popov A I 1985 *Rare-Earth Ions in Magneto-Ordering Crystals* (Moscow: Nauka)
[9] Bleaney B 1963 *Proc. R. Soc.* A **276** 19
[10] Frolova G I, Kozeeva L P and Paukov I E 1980 *Zh. Fiz. Chim.* **54** 336
[11] Kut'ko V I, Kharchenko Ju N, Nesterenko N M and Gurskas A A 1996 *Low Temp. Phys.* **22** 603