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2008 J. Phys.: Condens. Matter 20 395223

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Anisotropic magnetization of the Van Vleck paramagnet LiTmF_4 at low temperatures and high magnetic fields

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Received 19 June 2008, in final form 15 August 2008

Published 4 September 2008

Online at stacks.iop.org/JPhysCM/20/395223

Abstract

Lithium thulium fluoride LiTmF_4 is an insulating Van Vleck paramagnet with a giant magnetostriction. Magnetization of the tetragonal LiTmF_4 single crystals was measured for the first time in the temperature range of 2–300 K and in magnetic fields up to 55 kOe, oriented both parallel and perpendicular to the C_4 symmetry axis. In particular the angular dependence of the magnetization in the basal plane was studied. The anisotropy of magnetization in this plane grows rapidly in high fields. The temperature dependence of the magnetization in the orientation $\vec{H} \parallel [001]$ is nonmonotonic and reproduced very well by the calculation in the framework of the crystal field theory. The discrepancies between experimental and theoretical dependences in the orientation $\vec{H} \perp [001]$ in high magnetic fields are attributed to the magnetostriction effects.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic properties of the insulating paramagnet lithium thulium fluoride LiTmF_4 were studied by means of the nuclear magnetic resonance (NMR) in moderate magnetic fields up to 6.7 kOe in [1, 2]. In particular in [1] the effect of magnetostriction on the ^{169}Tm NMR spectra was studied and the anisotropy of the resonance field in basal plane was discovered. In [3] the magnetic properties of the powder samples were studied and sharp jumps of magnetization in high fields and low temperatures were observed. These jumps were attributed to the manifestation of field-induced phase transitions in LiTmF_4 . The magnetic susceptibility of the dilute single crystals $\text{Tm}^{3+}:\text{LiYF}_4$ was studied theoretically in [4, 5] but no magnetostriction effects were taken into account. In [6] the magnetic anisotropy of LiRF_4 ($R = \text{Tb, Dy, Ho, Er, Yb}$) crystals in the basal plane was studied. Recently the study of splitting of the first excited crystal field (CF) doublet $\Gamma_{34}^1(^3\text{H}_6)$ of the Tm^{3+} ion in $\text{LiY}_{1-x}\text{Tm}_x\text{F}_4$ ($0.02 \leq x \leq 1$) crystals in magnetic field was performed in [7] and

the optical spectroscopic method of magnetostriction detection was proposed.

LiTmF_4 crystal has a scheelite (CaWO_4) structure with the space group C_{4h}^6 . The unit cell contains two magnetically equivalent Tm^{3+} ions at sites with S_4 point symmetry. At low temperature LiTmF_4 exhibits a giant magnetostriction which was discovered by Altshuler *et al* [8]. Lattice distortion caused by the redistribution of the electronic density of magnetic ions achieves values of $\sim 10^{-3}$ in magnetic fields of 30 kOe perpendicular to the crystal symmetry axis (see figure 1(b)). Tm^{3+} ion in LiTmF_4 has the singlet ground state separated by a relatively small gap of 30 cm^{-1} from the first excited doublet Γ_{34}^1 , therefore LiTmF_4 is a Van Vleck paramagnet with relatively high magnetic susceptibility in the orientation $\vec{H} \perp [001]$.

Crystal deformation due to giant magnetostriction alters the wavefunctions and the energies of CF levels, thus affecting the magnetic susceptibility. To investigate this effect in detail we decided to study magnetic properties of LiTmF_4 in low temperatures and high magnetic fields because in these

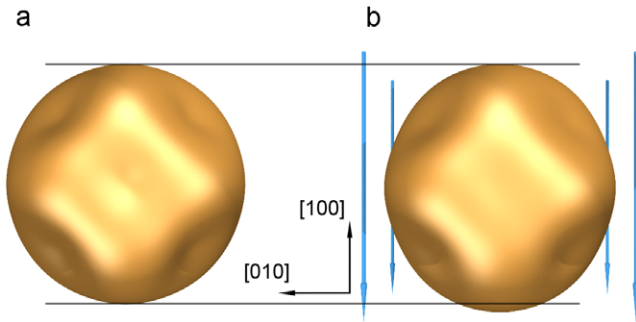


Figure 1. Isosurfaces of 4f-electronic density of Tm³⁺ ion in LiTmF₄; (a) without applied magnetic field; (b) in a magnetic field of 55 kOe in the orientation $\vec{H} \parallel [100]$. In case (b) the electron distribution is elongated by about 3% in the \vec{H} direction and compressed in direction normal to it by the same value. Wavefunctions used to draw these pictures were obtained by using the effective Hamiltonian reported in [7]. The animation file (available at stacks.iop.org/JPhysCM/20/395223) shows the distortion process starting from frame (a) and ending on frame (b) while magnetic field is increased uniformly in time.

conditions the magnetostriction is particularly strong. In this paper we present the results of our measurements and calculations on the magnetization dependences M_{\parallel} and M_{\perp} of LiTmF₄ single crystal over the temperature range of 2–300 K and magnetic fields up to 55 kOe.

2. Experimental details

The crystal for investigation was grown by the Bridgman–Stockbarger method and was of a good optical quality. Samples for experiments were prepared from this grown crystal. Orientation along the symmetry axis [001] was controlled by the polarizing microscope, and the directions of the [100] and [010] axes were found using the x-ray diffractometer. Axes [100] and [010] are indistinguishable. For the magnetization measurements a DC SQUID magnetometer MPMS by Quantum Design was used. It is designed to measure magnetic moments up to 1.25 emu. Preliminary measurements of LiTmF₄ in order to estimate the magnetic moment in maximal field suggested that we use a sample of about only 10 mg in weight and in the measurements of M_{\perp} to avoid the exceeding of the instrument’s range. It is difficult to preserve the orientation of such a small sample. Therefore it was decided to make the sample of a parallelepiped shape of 1.5 mm × 1.5 mm × 0.9 mm in size. The larger face was normal to the symmetry axis [001] (figure 2) and was glued by epoxy resin to the flat bottom of the sample holder, which was oriented parallel to magnetic field. The increased area of the sample face which was glued to the sample holder, allowed us to better preserve the correct orientation $\vec{H} \perp [001]$. In order to allow the sample freedom to change its size due to magnetostriction, only a small amount of epoxy resin was used. The shape of our sample leads to an increase of the local field at Tm³⁺ ions in the orientation $\vec{H} \perp [001]$ by 2%. Experimental results were corrected by this value. In the measurements of

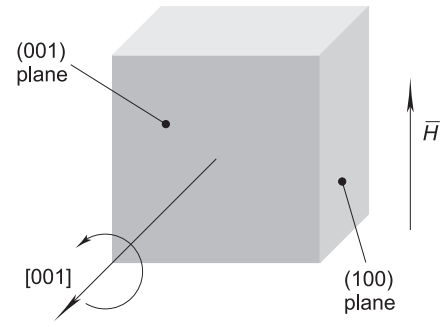


Figure 2. Geometry of the experiment. The LiTmF₄ sample is rotated about its [001] crystallographic axis while the magnetic field \vec{H} is parallel to (001) plane.

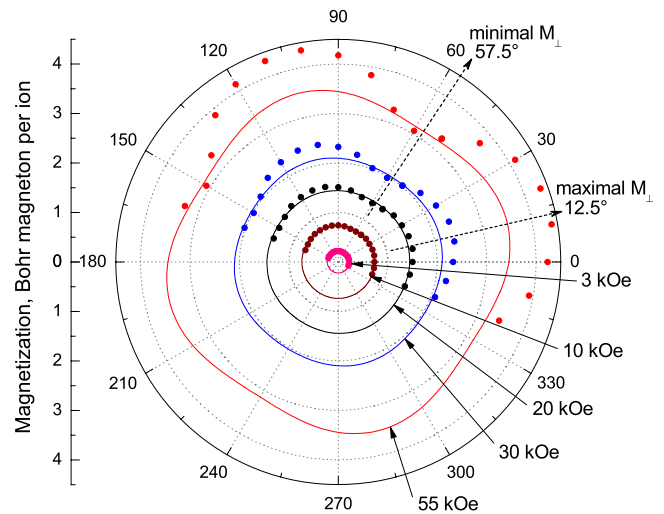


Figure 3. Angular dependences of LiTmF₄ magnetization at various magnetic fields $\vec{H} \perp [001]$. Temperature is 4.2 K. Symbols (●): experimental data; lines (—): results of calculation. In all the cases the experimental points which are nearest to the calculated curve were obtained at the same field as this curve was calculated for.

the angular dependence of M_{\perp} , the sample was rotated in the (001) plane with an accuracy of $\pm 1^{\circ}$. The geometry of the experiment is outlined in figure 2. Since at liquid helium temperatures the susceptibility χ_{\parallel} is about 40 times smaller than χ_{\perp} , we used a cubic sample of much larger mass (about 400 mg) in experiments in the orientation $\vec{H} \parallel [001]$.

3. Results

The angular dependences of magnetization M_{\perp} in various magnetic fields are presented on figure 3, where the magnetic field direction is defined by an angle φ , measured from the crystallographic axis [100]. The maximum magnetic field used was 55 kOe. One can see that magnetic anisotropy in (001) plane rapidly increases with magnetic field. The maximum and minimum of M_{\perp} are reached at angles $\varphi_{\max} \approx 12.5^{\circ} + 90^{\circ} \cdot n$ and $\varphi_{\min} \approx 57.5^{\circ} + 90^{\circ} \cdot n$, respectively.

It can be seen from figure 4 that at liquid helium temperatures in the orientation $\vec{H} \perp [001]$, φ_{\max} the susceptibility increases with magnetic field and reaches a

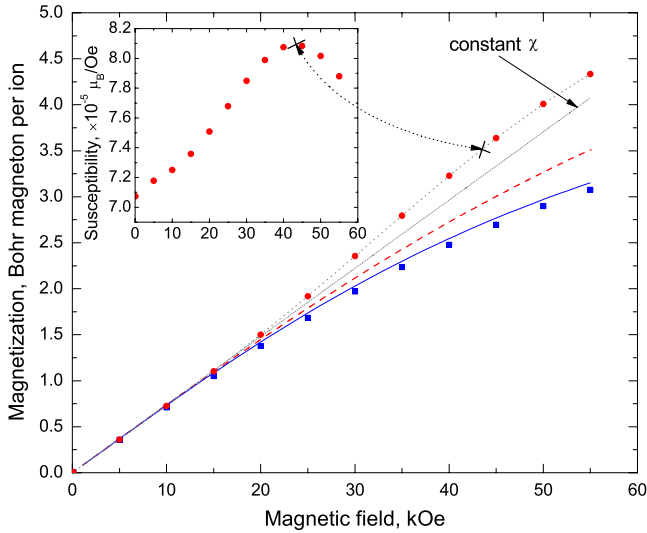


Figure 4. Magnetic field dependences of LiTmF₄ magnetization in the orientation $\vec{H} \perp [001]$. Temperature is 4.2 K. Symbols correspond to the experimental data; (■): $\varphi = 57.5^\circ$; (●): $\varphi = 12.5^\circ$. Lines are results of calculation; (—): $\varphi = 57.5^\circ$; (- - -): $\varphi = 12.5^\circ$. In the experiment the maximum susceptibility χ_{\perp} (defined as magnetization per ion divided by magnetic field strength) is reached at field ≈ 43.5 kOe for $\varphi = 12.5^\circ$ (shown in the inset).

maximum at ≈ 43.5 kOe, while in the direction of minimal magnetization it decreases monotonically.

Experiments showed that in the orientation $\vec{H} \parallel [001]$ susceptibility is independent of magnetic field up to 55 kOe.

Temperature dependences were measured in two orientations: in the (001) plane for $\varphi = \varphi_{\max}$ and φ_{\min} , i.e. in the orientation of minimum susceptibility in this plane, and in the orientation $\vec{H} \parallel [001]$. In accordance with the results of calculations for dilute crystals [4, 5], the experiments on LiTmF₄ in the present work showed that magnetization below 8 K is temperature-independent (figures 5, 6). This is the distinctive feature of the Van Vleck paramagnets. In the orientation $\vec{H} \parallel [001]$ the temperature dependence of magnetization is nonmonotonic (figure 6), and this is also a frequently displayed feature of the Van Vleck paramagnets in the orientation of the minimal susceptibility, since magnetic ions in the excited CF states usually have larger magnetic moments. The temperature independence of the magnetization below 8 K shows that there is only an insignificant amount of impurities, i.e. sources of conventional paramagnetism in our samples.

4. Analysis and discussion

In our calculations we worked only in space of the ground multiplet of the ground $4f^{12}$ electron configuration of the free Tm³⁺ ion $|^3H_6\rangle = 0.9953|^3H_6\rangle + 0.0973|^1I_6\rangle$ (table IV in [9]). The energy-level pattern of the single Tm³⁺ ion in the LiTmF₄ crystal field and in the external magnetic field \vec{H} can be described by the Hamiltonian

$$H = \alpha B_2^0 O_2^0 + \beta (B_4^0 O_4^0 + B_4^4 O_4^4 + B_4^{-4} O_4^{-4}) + \gamma (B_6^0 O_6^0 + B_6^4 O_6^4 + B_6^{-4} O_6^{-4}) + g_J \mu_B \mathbf{JH}, \quad (1)$$

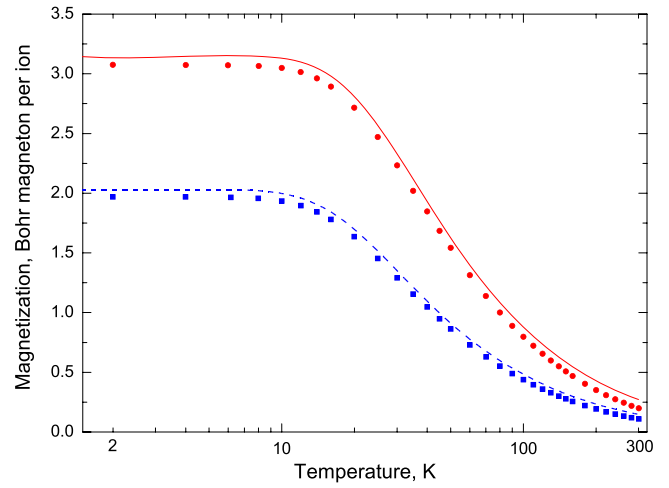


Figure 5. Temperature dependences of LiTmF₄ magnetization in the orientation $\vec{H} \perp [001]$, $\varphi = 57.5^\circ$. Symbols correspond to experimental data; (●): $H = 55$ kOe; (■): $H = 30$ kOe. Lines are the results of the calculation; (—): $H = 55$ kOe; (- - -): $H = 30$ kOe.

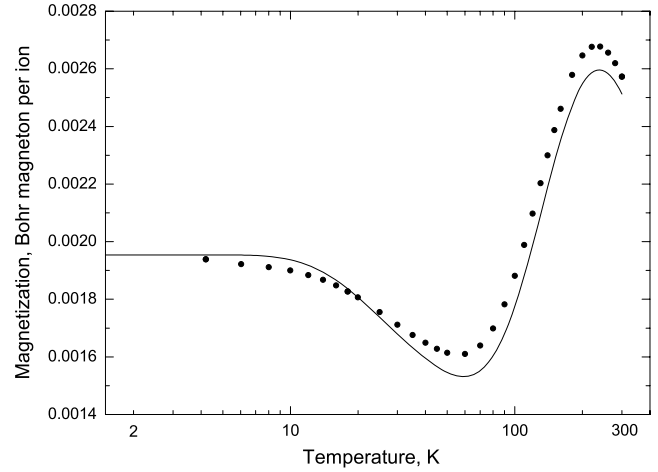


Figure 6. Temperature dependence of LiTmF₄ magnetization. $\vec{H} \parallel [001]$, $H = 1$ kOe. Symbols (●): experimental data; line (—): result of calculation.

where α , β and γ are the reduced matrix elements of real and imaginary Stevens operators O_p^k , Ω_p^k , respectively ($\alpha = 1/99 \cdot 1.0096$, $\beta = 8/(81 \cdot 5 \cdot 121) \cdot 0.9764$, $\gamma = -5/(81 \cdot 7 \cdot 121 \cdot 13) \cdot 0.9868$); B_p^k are the crystal field parameters. We used the CF parameters determined in [10] (see table III, column 1 there) from experimental data on LiTmF₄ optical spectra. These parameters were corrected in [7] ($B_4^{\pm 4}$ were diminished by 8%) to fit the maximum Zeeman splitting of the first excited crystal field doublet. In the present work the parameters $B_4^{\pm 4}$ and $B_6^{\pm 4}$ were renormalized in order to fit the positions of the maxima of the angular dependence of M_{\perp} to those of experimental data. The resulting CF parameters are: $B_2^0 = 184$, $B_4^0 = -90$, $B_6^0 = -4.06$, $B_4^4 = -570.6$, $B_4^{-4} = -675.2$, $B_6^4 = -280.1$ and $B_6^{-4} = -331.5$ cm⁻¹. The last term in (1) is the Zeeman energy (the Lande factor $g = 7/6 \cdot 0.9987$, μ_B is the Bohr magneton, and \mathbf{J} is the total angular momentum).

The energies and wavefunctions of the Tm^{3+} ion in the LiTmF_4 crystal in a magnetic field were obtained by using the numerical diagonalization of the matrix of Hamiltonian (1) in the space of 13 states of the ground $^3\text{H}_6'$ multiplet. The calculated dependences of the magnetization are presented in figures 3, 4, 5 and 6.

It can be seen from figures 3, 4 and 5 that in directions of minimum M_{\perp} , i.e. $\vec{H} \perp [001]$, φ_{\min} the calculated dependences agree well with experimental data (deviation does not exceed 2%). In [7] a method of calculation of the effective Hamiltonian which takes into account the magnetostriction was proposed. Using that Hamiltonian, we found that in the orientations $\vec{H} \perp [001]$, φ_{\min} the macrodeformation (i.e. the change of the dimensions of the unit cell and, therefore, the whole crystal) decreases to only 5% of that in the $\vec{H} \perp [001]$, φ_{\max} orientations. In this direction the crystal deformation due to magnetostriction affects the magnetization very weakly (the contribution is only 0.5% according to calculations). Therefore it is enough to take into account only Zeeman and crystal field interactions in order to get a good agreement for this orientation. On the contrary, in strong fields in the directions of the maximum M_{\perp} , i.e. $\vec{H} \perp [001]$, φ_{\max} there are significant, and growing with field, deviations between the calculated dependences and experimental data (figures 3, 4). These deviations are fully attributed to the effect of magnetostriction.

It was established in [2] that a single-ion mechanism of magnetostriction is dominant in LiTmF_4 crystal. The Zeeman energy $E = -\vec{M}\vec{H}$ of polarized 4f-electronic shell of Tm^{3+} ion in applied magnetic field is dependent on crystal deformation through an electron-lattice interaction. Crystal deformation alters the crystal electric field which influences the electronic density distribution of Tm^{3+} 4f shell. The distortion of electronic density distribution alters the ionic wavefunction, which defines the mean value of the magnetic moment of the Tm^{3+} 4f shell. This magneto-elastic coupling accounts for the magnetostriction in LiTmF_4 as well as for inverse phenomena—the effect of crystal deformation on its magnetic properties.

The sample deformation in the orientation $\vec{H} \perp [001]$ increases rapidly with increasing field. The dependence of deformation on the field as well as the magnetization oscillation depth are described by a quadratic function [2, 8], therefore the disagreement in the orientation of $\vec{H} \perp [001]$, φ_{\max} grows rapidly (figures 3, 4). Deformation of LiTmF_4 crystal due to magnetostriction contributes significantly to the anisotropy of magnetization in the (001) plane. One can see the magnitude of this contribution as well as its field dependence by comparing the measured and calculated data in figure 3, bearing in mind that calculated data corresponds to non-deformed sample. In the early experiments with LiTmF_4 we observed significantly decreased magnetic anisotropy in the basal plane when the sample was fixed entirely inside the epoxy resin and could not freely change its shape.

There is no magnetostriction in the orientation $\vec{H} \parallel [001]$ [8], since in this case the excited CF levels which can be admixed to the ground level have very high energies. Therefore there is a good agreement between our calculated and experimental data for this orientation.

5. Conclusion

Magnetization of the single crystal Van Vleck paramagnet LiTmF_4 was measured for the first time in the temperature range of 2–300 K and in magnetic fields up to 55 kOe oriented both parallel and perpendicular to the C_4 symmetry axis. The anisotropy of the magnetization in the basal plane grows rapidly in high fields. The temperature dependence of the magnetization in the orientation $\vec{H} \parallel [001]$ was nonmonotonic and reproduced very well by the calculation in the framework of the crystal field theory. The discrepancies between experimental and theoretical dependences in the orientation $\vec{H} \perp [001]$ in high magnetic fields are attributed to the magnetostriction effects.

It is known as a remarkable feature of the Van Vleck paramagnets that NMR of nuclei of paramagnetic ions can be observed at low temperatures. NMR of ^{169}Tm can be used to probe the magnetic moment of 4f shell of Tm^{3+} ions in LiTmF_4 . In [1] it was found experimentally that the direction of the maximum effective gyromagnetic ratio of the ^{169}Tm nuclei in LiTmF_4 crystal in the (001) plane corresponds to the angle $\varphi \sim 11^\circ$ between the [100] axis and the magnetic field directions. This result is in good agreement with the value of $\varphi_{\max} = 12.5^\circ$ for the direction of the maximum magnetization determined in present work.

It is clear from figure 4 that no structural phase transitions which affect LiTmF_4 magnetization occur in the magnetic field range used. This suggests to us to propose that the sharp jumps of the magnetization of the powder samples in [3] in the magnetic fields above 40 kOe occurred due to size effect.

Acknowledgments

The authors would like to thank Professor B Z Malkin for his constant interest in this work and for making valuable comments, S L Korableva for growing the crystal and V A Shustov for performing the orientation of this crystal by means of x-rays.

References

- [1] Al'tshuler S A, Kudryashov A A, Teplov M A and Terpilovskii D N 1982 *JETP Lett.* **35** 299
- [2] Al'tshuler S A, Malkin B Z, Teplov M A and Terpilovskii D N 1985 *Soviet Scientific Reviews, Section A, Physics Reviews* vol 6, ed I M Khalatnikov (New York: Harwood Academic) p 61
- [3] Klochkov A V, Naletov V V, Mukhamedshin I R, Tagirov M S, Tayurskii D A and Suzuki H 1997 *JETP Lett.* **66** 266
- [4] Kumar V, Vishwamittar and Chandra K 1977 *J. Phys. C: Solid State Phys.* **10** 267
- [5] Chen X Y and Luo Z D 1997 *J. Phys.: Condens. Matter* **9** 4197
- [6] Nevald R and Hansen P E 1977 *Physica B* **86–88** 1443
- [7] Abdulsabirov R Y, Kazantsev A A, Korableva S L, Malkin B Z, Nikitin S I and Stolov A L 2006 *J. Lumin.* **117** 225
- [8] Al'tshuler S A, Krotov V I and Malkin B Z 1980 *JETP Lett.* **32** 214
- [9] Krupke W F 1965 *Phys. Rev.* **139** A2008
- [10] Christensen H P 1979 *Phys. Rev. B* **19** 6573