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CRYSTAL FIELD OF RARE-EARTH ION IN TmFeO

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The crystal field parameters related to Tm^{3+} ion in $TmFeO_3$ have been determined. This gives a possibility to evaluate a contribution of RE subsystem to different properties of this compound, iucluding influence of high pressure.

The propeties of $TmFeO_3$ as those of any other rare-earth (RE) compound at low temperatures are essentially determined by the RE subsystem. Peculiarities of the RE ion electron structure formed by its interaction with the crystal environment (crystal field) define the distinct features of the RE compound. For $TmFeO_3$ they are the spontaneous spin reorientation ($\Gamma_4 \leftrightarrow \Gamma_2$) at $T < 100$ K and very intereasting magnetic properties of the low-temperature phase $\Gamma_2(F_xG_z)$ (see e.g. [1]). A non Kramers ion Tm^{3+} in the orthoferrite shows a set of singlet energy levels, splitted by the crystal field (CF) of the C_s symmetry. The lower part of ground multiplet known from the optical absorption spectra [2] is very useful for understanding of a great number of the $TmFeO_3$ properties. But wave fanctions are also desired, for example to calculate the oscillator strength for the transitions between levels within the ground multiplet recently investigated in $TmFeO_3$ [3] .

In this work we present the temperature dependences of a magnetic susceptibility of $TmFeO_3$ measured along the three crystal axes in 0.68...300 K temperature range. These data together with the available information on splittings of 4 multiplets of the Tm^{3+} ion in $TmFeO_3$ were used to determine the CF parameters.

The susceptibility measurements at T > 4.2 K were carried out by vibrating sample magnetometer, below 4,2 K the induction methods were used (the frequency of modulation dozens Hz). Both methods give the same values for the magnetic susceptibility being far from the order phase transitions [4]. In Fig. 1 the data obtained for the temperature dependences of the inverse susceptibility $\chi^{-1}(T)$ of $TmFeO_3$ along a,b and c axes are shown. Continuous curves represent the theoretical dependences of $\chi^{-1}(T)$ calculated for the CF parameters, determined fitting the experimental and

calculated values for magnetic susceptibility data and splitting and representation labels for four Tm^{3+} ion multiplets [2].

Stark splittings of multiplets were calculated with the CF Hamiltonian of C_s symmetry

$$H_{CF} = \sum_{k,q} \left\{ \mathrm{Re}\, B_q^k \left(C_q^k + C_{-q}^k \right) + i\, I_m B_q^k \left(C_q^k - C_{-q}^k \right) \right\} \qquad (1)$$

with fifteen CF parameters B_q^k (see [5] e.g.). For closely-lying multiplets ^3Fj ($j = 4,3,2$) j-mixing has been taken into account. The calculation has been performed with wave functions of free ion obtained in the intermediate coupling approximation, it is especially essential in the case of $^3F_4$ multiplet which is called $^3H_4$ in modern designation [7] due to a great contribution of corresponding wave functions.

The magnetic susceptibility of Tm^{3+} ions along the crystal axes was calculated with the usual formula

$$\chi_\alpha = \frac{2 g_J^2 \mu_B^2 N}{Z} \sum_n e^{-E_n/k_B T} \sum_{m \neq n} \frac{\left| \langle n | J_\alpha | m \rangle \right|^2}{E_m - E_n},$$

where the Lande factor $g_J = 7/6$, N the number of Tm^{3+} ions in 1 g,

$$Z = \sum_{n=3}^{13} e^{-E_n/k_B T}$$, E_n and $|n>$ are energy levels and wave functions of the ground multiplet respectively.

For the starting values in optimization we have used the CF parameters for Tm^{3+} in $YAlO_3$, determined in [8] with the descending symmetry technique in crystallographic coordinate system. An often used method [9] in which these parameters are determined in the coordinate system, where $\mathrm{Im} B_2^2 = 0$ (only 14 from 15 parameters are independent) is not suitable in those cases, when not only Stark splittings but the parameters of (in cm^{-1}) $B_0^2 = -575$, $B_0^4 = 163$, $B_0^6 = 10$, $\mathrm{Re} B_2^2 = -142$, $\mathrm{Re} B_2^4 = 103$, $\mathrm{Re} B_2^6 = 373$, $\mathrm{Re} B_4^4 = 368$, $\mathrm{Re} B_4^6 = 245$, $\mathrm{Re} B_6^6 = -443$, $\mathrm{Im} B_2^2 = -152$, $\mathrm{Im} B_2^4 = 580$, $\mathrm{Im} B_2^6 = 767$, $\mathrm{Im} B_4^4 = 498$, $\mathrm{Im} B_4^6 = 400$, $\mathrm{Im} B_6^6 = -331$. For these parameters known splitting of the ground multiplet $^3H_6$ are reproduced within the experimental errors of [2]. The matrix element $<1|\mu_B g_J J_z|2> = (4.05\pm0,25)\,\mu_B$ evaluated in [2] from Zeeman effect is 4.20 μ_B. Splittings of three exited multipletes are not described quantitatively, but the distinct features are reproduced, such as sequences of level representations, the whole splittings of each multiplet, some of characteristic peculiaties like the existence of a quasidoublet in a lower part of the $^3F_3$ multiplet, etc. Fig.1 shows that the magnetic susceptibility data are described sufficiently well.

The determined electron structure of the Tm^{3+} ion in $TmFeO_3$ gives a possibility to evaluate a contribution of RE subsystem to the different properties of this compound.
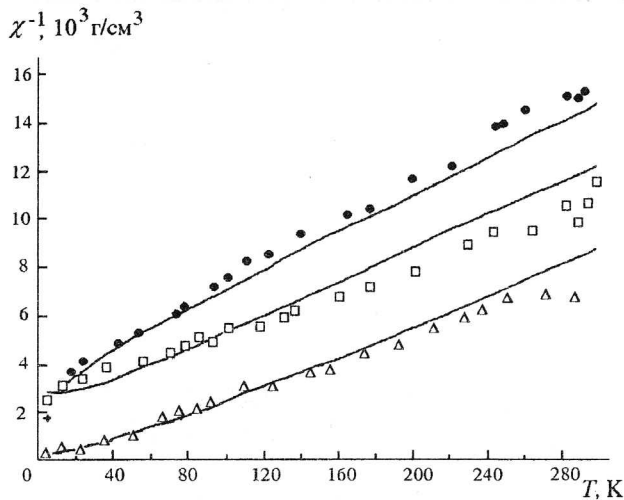
$\chi^{-1}, 10^3$ г/см^3

Fig.1 Temperature dependences of the inverse magnetic susceptibility $1/\chi$ along the three crystal axes in $TmFeO_3$. Solid lines are theoretical curves, symbols are experimental points along b-axis (●), a-axis (□), c-axis (Δ)

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