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Magnetic properties of a mixed-valence (III/IV) terbium fluoride KTb_3F_{12}

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The mixed-valence terbium (III/IV) fluoride KTb_3F_{12} crystallizes with the tetragonal symmetry, space group $I4/m$. Below $T_N = 3.6 \pm 0.1$ K this compound exhibits an antiferromagnetic collinear structure with $k = 0$ characterized by ferromagnetic chains of edge-sharing Tb^{4+} polyhedra and an antiferromagnetic order between the nearest chains. The magnetic moments of the Tb^{4+} ions deduced from neutron diffraction are equal to 6.95(4) μ_B at 1.4 K and aligned along the c axis. The Tb^{3+} ions lie in a special position with zero magnetic moments due to a symmetry cancellation effect of the internal molecular field. In other words, Tb^{3+} ions present a zero time-averaged magnetic moments in the ordered state, whereas T_N corresponds to the long-range antiferromagnetic ordering of the moments of the Tb^{4+} ions. From the thermal variation of the reciprocal magnetic susceptibility a molar Curie constant of 27.97(1) emu K mol^{-1} has been obtained, in good agreement with the theoretical value of 27.64 expected for two Tb^{4+} and one Tb^{3+} free ions. The Tb^{4+} contribution to the magnetization is approximated by the Langevin function and then the Tb^{3+} contribution is obtained by subtracting the calculated Tb^{4+} contribution to the total magnetization.
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I. INTRODUCTION

Recently, a mixed-valence III/IV terbium fluoride KTb_3F_{12} resulting from the partial thermal decomposition of the terbium tetrafluoride at high temperature that yields trivalent terbium fluoride, even under fluorine atmosphere, has been evidenced. The crystal structure of this compound considered as the archetype of a large family of related $KLn^{III}M_2{}^{IV}F_{12}$ compounds ($Ln^{III} = Ce \rightarrow Lu; M^{IV} = Tb, Zr, Hf$) has been determined from single-crystal x-ray and powder neutron diffraction study.[1] It is characterized by the presence of chains of edge-sharing $(TbF_8)^{4-}$ dodecahedra further linked by isolated Tb^{3+} ions alternating with K^+ ones along the c direction. This polyhedral string was, *a priori*, favorable to the apparition of superexchange magnetic interactions at low temperature.

This work deals with the study of the magnetic properties of this compound between 1.6 and 300 K under high continuous magnetic field up to 200 kOe and its magnetic structure determined from neutron powder diffraction below 3.6 K showing an unexpected ''idle spin'' behavior of the Tb^{3+} ions below this temperature and down to 1.4 K.

II. EXPERIMENT

Polycrystalline samples of KTb_3F_{12} were obtained by heating overnight, at 650 °C, stoichiometric mixtures of dehydrated KCl and TbF_4 in a nickel boat under pure fluorine atmosphere. To obtain a pure sample, the sample weight must not exceed about 1.2 g so several batches were necessary to prepare the whole sample used in neutron diffraction experiments. Therefore, an annealing of the whole sample has been carried out in the same conditions, i.e., at 650 °C, overnight, under a pure fluorine gas flow, in order to obtain a homogeneous powder.

Magnetic measurements over the temperature range 1.6–300 K were carried out at the High Magnetic Field Laboratory in Grenoble, on polycrystalline samples, using an automatic device.[2] The extraction technique was used to measure the magnetic moment in continuous magnetic fields up to 200–230 kOe.[3]

Neutron diffraction patterns were recorded at the Orphee reactor (Saclay, France) on the 3T2 high resolution powder diffractometer ($\lambda = 1.2259$ Å) for the determination of the

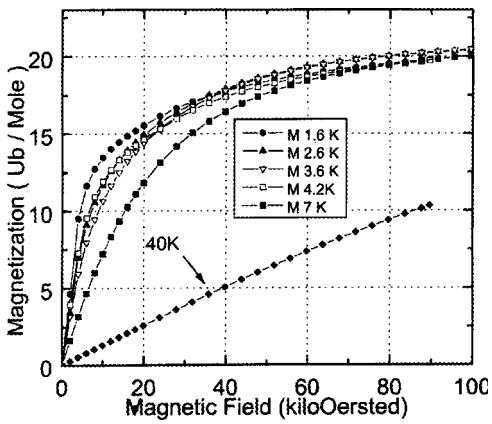

FIG. 1. Applied magnetic field dependence of the magnetization for KTb_3F_{12} at low temperature.

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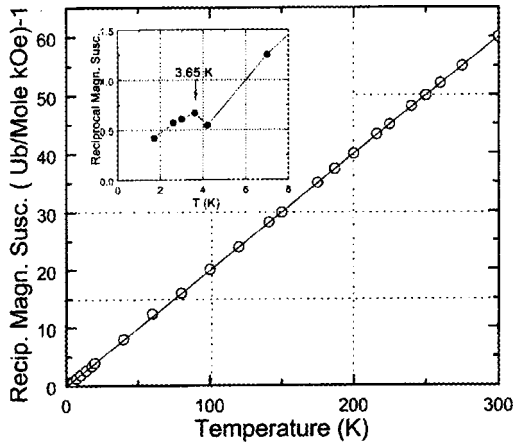

FIG. 2. Temperature dependence of the reciprocal susceptibility of KTb_3F_{12}. The inset shows the details of the 1.6–7 K low temperature range data.

nuclear structure in the 5–300 K temperature range and then between 1.4 and 4.2 K on the two-axis diffractometer G4.1 ($\lambda = 2.426$ Å) for the determination of the magnetic structure.[4] The data were analyzed with the FULLPROF program.[5]

III. RESULTS AND DISCUSSION

The crystal structure of KTb_3F_{12} has been determined by single-crystal x-ray diffraction but the true space group (*I4/m*, No. 87) was chosen[1] in the light of the already available neutron diffraction results presented here. Indeed the Rietveld refinement of the structure from the neutron diffraction powder pattern recorded at room temperature using the FULLPROF program[5] ($R_{Bragg} = 0.049$) showed that the true symmetry is *I4/m* rather than *I4/mmm* and that the crystal studied by x-ray diffraction was twinned.

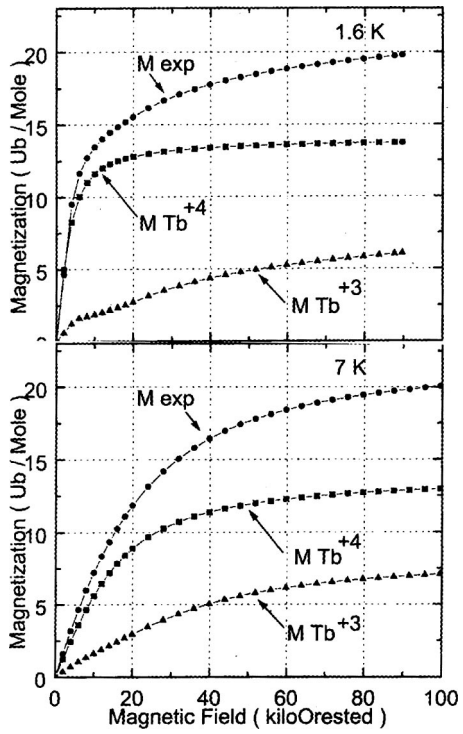

FIG. 3. Evaluation of the applied field dependencies of the magnetization of both Tb^{3+} and Tb^{4+} ions at 1.6 and 7 K, respectively.

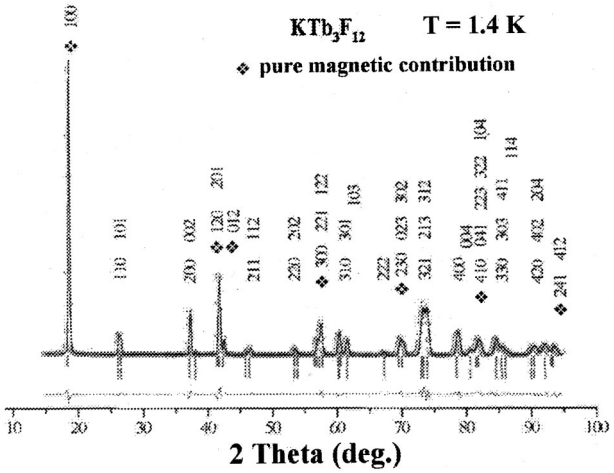

FIG. 4. Observed, calculated and difference neutron diffraction powder patterns of KTb_3F_{12} in the magnetically ordered state at 1.4 K.

A. Magnetic properties

The magnetization M exhibits a linear applied field dependence above 40 K (Fig. 1). When the temperature decreases from 40 to 1.6 K, the $M(H)$ curves present a more and more pronounced curvature. Isothermal zero-field and maximum-field cooling curves were found rigorously identical and no hysteresis phenomena were observed.

The initial magnetic susceptibility χ was deduced from the fit of the initial part of the $M(H)$ curve corresponding to the linear H variation (i.e., 0–6 kOe below 10 K). The temperature dependence of the reciprocal magnetic susceptibility between 1.6 and 300 K is reported in Fig. 2. Above 12 K the thermal variation of the susceptibility obeys a Curie–Weiss-type law $\chi^{-1} = (T - \theta_p)/C$. The paramagnetic temperature is very close to zero since found equal to (-0.75 ± 0.10) K.

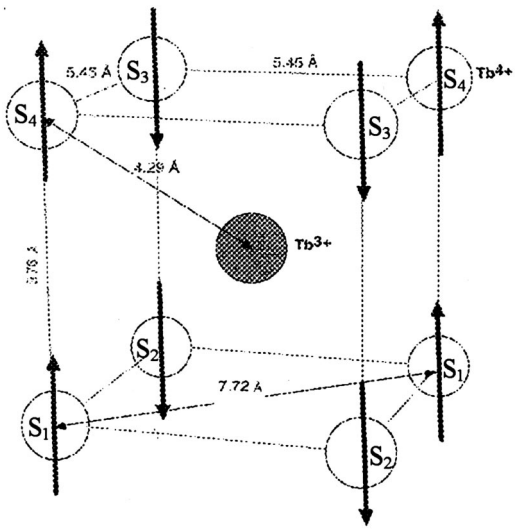

FIG. 5. Arrangement of the Tb^{4+} magnetic moments aligned along the *c* axis of the KTb_3F_{12} structure.

TABLE I. Coordinates of magnetic cations Tb^{4+} (site $4d$) and Tb^{3+} (site $2b$) in the space group *I4/m* (No. 87) and refined magnetic components (in μ_B) at 1.4 K for KTb_3F_{12}.

Atoms and spins	Atomic coordinates			Magnetic components		
	x	y	z	M_x	M_y	M_z
$Tb^{4+}(S_1)$	1/2	0	1/4	0	0	6.95(4)
$Tb^{4+}(S_2)$	0	1/2	1/4	0	0	−6.95(4)
$Tb^{4+}(S_3)$	0	1/2	−1/4	0	0	−6.95(4)
$Tb^{4+}(S_4)$	1/2	0	−1/4	0	0	6.95(4)
$Tb^{3+}(S_1)$	1/2	1/2	0	0[a]	0[a]	0[a]

[a]Undetermined value due to the "idle spin" behavior.

The Curie constant $C=27.97\pm0.01$ emu K mol^{-1} is in good agreement with the value calculated for two Tb^{4+} and one Tb^{3+} free ions.

At very low temperature (see inset in Fig. 2) a weak maximum of χ^{-1} is observed at 3.65 ± 0.1 K. This behavior was unambiguously confirmed for the different studied samples. Neutron diffraction experiments (see Sec. III B) confirm that this temperature should be considered as a Néel point. It should be noted that below T_N, there is no spontaneous magnetization and that all the $M(H)$ curves, below 3.65 K, exhibit the same trend as that above T_N. Comparison of the 1.6 and 4.2 K curves reveals that the magnetization at 1.6 K is only slightly higher than that at 4.2 K.

When H is higher than about 20 kOe, the contribution of the Tb^{4+} sublattice originates from the applied field-induced orientation of the ferromagnetic independent grains whose magnetization is 14 μ_B (Tb^{4+}: $4f^7$ electronic configuration, $^8S_{7/2}$ ground state value); it is given, in a first approximation, by the corresponding Langevin function. The contribution of the Tb^{3+} sublattice is then determined from the difference between the experimental $M(H)$ variation and the Tb^{4+} contribution calculated using the Langevin function. As shown in Fig. 3, the contribution to the total magnetization of the Tb^{3+} ions is important except in very low field. To support the above interpretation, it should be noted that the simple application of the Néel theory of antiferromagnetism to the experimental values of C and θ_p leads to a molecular field on each Tb^{4+} ion equal to about 9 kOe.

B. Magnetic structure at 1.4 K

From the examination of the neutron diffraction powder patterns recorded at various temperatures it has been observed that pure magnetic peaks appear below 3.6 K (Fig. 4). From the thermal variation of the integrated intensity of the (1 0 0) more intense magnetic peak the Néel temperature has been found to be equal to about 3.65 K. All the magnetic peaks could have been indexed with the nuclear cell but the possible reflections show the magnetic cell to be primitive instead of body centered. The magnetic structure, determined using Bertaut's method,[6] may be described in the magnetic group I_p4'/m and the Tb^{3+} ions lie on the primed fourfold axis $4'_z$, so that the magnetic moment of the Tb^{3+} ions should be equal to zero.[7,8] The refined values of the magnetic moments components of the Tb^{4+} ions are gathered in Table I. The collinear antiferromagnetic structure observed below 3.6 K (Fig. 5) results from ferromagnetic coupling between the Tb^{4+} ions within the chains of edge-sharing $(TbF_8)^{4-}$ dodecahedra and an antiferromagnetic arrangement between the nearest chains in a tetragonal packing. The T_N temperature corresponds in this case to the long-range ordering of the Tb^{4+} magnetic moments. Whatever the sign of the $Tb^{4+}-F-Tb^{3+}$ superexchange interaction, the Tb^{3+} ion lies in a special position that does not exhibit ordered magnetic moments due to the exact compensation between the eight interactions acting on the Tb^{3+} ion (Fig. 5). Under zero applied magnetic field which is the experimental condition for neutron diffraction pattern recording, the time average of the magnetic moments is observed to be equal to zero (idle spin behavior). In other words, the Tb^{3+} magnetic moments remain in the paramagnetic state, whereas the Tb^{4+} sublattice is magnetically ordered.

IV. CONCLUSION

Below 3.6(1) K, the mixed-valence terbium (III/IV) fluoride KTb_3F_{12} exhibits a collinear antiferromagnetic structure resulting from antiferromagnetic couplings between ferromagnetic nearest chains via F^- and Tb^{3+} ions involved in superexchange. The magnetic moment modulus of the Tb^{4+} ion determined experimentally, at 1.4 K, from neutron powder diffraction analysis, has been found to be very close to the ideal value ($\mu_{exp}=6.95(4)\mu_B$, $\mu_{th}=7\mu_B$). High magnetic field magnetization measurements confirm this value as well as the coexistence of both III and IV oxidation states in KTb_3F_{12}. Surprisingly, the Tb^{3+} magnetic moments remain in the paramagnetic state due to the symmetry-induced total compensation of the molecular field of the Tb^{4+} sublattice acting on the Tb^{3+} site and therefore exhibits an idle spin behavior. More details concerning this study will be published in a forthcoming article.

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