Crystal structure and magnetic properties of the RCu$_3$Te$_3$ (R = Er and Tm) compounds

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Abstract

The crystal structures of the RCu$_3$Te$_3$ (R = Er and Tm) compounds (space group $Pmn2_1$, Pearson symbol $oP28$) were determined by means of X-ray powder diffraction: $a = 1.26784(6)$ nm, $b = 0.76161(3)$ nm, $c = 0.69016(3)$ nm, $R_{Bragg} = 0.0814$ for ErCu$_3$Te$_3$; $a = 1.26756(3)$ nm, $b = 0.76053(2)$ nm, $c = 0.69034(2)$ nm, $R_{Bragg} = 0.0639$ for TmCu$_3$Te$_3$. The Te atoms are stacked in a close-packed arrangement with layers in the sequence AB. The R atoms occupy one-third of octahedral interstices, whereas the Cu atoms occupy half of tetrahedral interstices. Both compounds are Curie–Weiss paramagnets with no magnetic ordering down to 1.9 K.
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1. Introduction

In the course of our systematic investigation on rare-earth chalcogenides with transition metals we reported recently on the formation of the R$_7$Cu$_3$Te$_{12}$ (R = Er and Tm) compounds, which crystallize with a rhombohedral structure of the Ho$_7$Cu$_3$Te$_{12}$ type (space group $R\bar{3}m$) [1]. Other known phases in these two ternary systems are the RCuTe$_2$ compounds with the ErCu$_3$S$_3$ type crystal structure (space group $P\bar{3}$) [2]. Here we communicate for the first time on the existence of the RCu$_3$Te$_3$ ternaries that have orthorhombic unit cells characterized by space group $Pmn2_1$. The crystal structures of the new compounds have been refined from X-ray powder diffraction data, and moreover some basic magnetic characteristics of both phases have been determined in wide ranges of temperature and magnetic field.

2. Experimental details

Samples of ErCu$_3$Te$_3$ and TmCu$_3$Te$_3$ were prepared by sintering the elemental constituents of the nominal purity of 99.9 wt.%. The ingredients were taken in the stoichiometric ratios, sealed in evacuated silica tubes, and placed in a resistance furnace. The ampoules were heated with a rate of 30 K/h up to 1420 K and then kept at this temperature for 4 h. Afterwards the samples were cooled slowly (10 K/h) down to 870 K and annealed at this temperature for 240 h. After such a heat treatment the ampoules were quenched in cold water.

X-ray powder diffraction patterns were recorded using a DRON-4-13 powder diffractometer using Cu Kα radiation within a 2Θ range from 10° to 100° (step scan mode with a step size of 0.05° and counting time of 20 s per data point). Crystal structure determinations were performed using the CSD [3] program.

Magnetic measurements were carried out on powder specimens in the temperature range 1.9–400 K and in magnetic fields up to 5 T employing a Quantum Design MPMS-5 SQUID magnetometer.

3. Results and discussion

3.1. Crystal structure

The X-ray powder diffraction patters of ErCu$_3$Te$_3$ and TmCu$_3$Te$_3$ were conclusively indexed on the basis of primitive orthorhombic unit cells with the lattice parameters listed in Table 1. The systematic extinctions were found to be consistent with the space group $Pmn2_1$. Assuming this symmetry and using direct methods and difference Fourier syntheses we were able to extract for both compounds plausible structural models that account for the observed X-ray intensities. The crystal data and refinement information are summarized in Table 1, whereas the experimental and calculated diffractograms and the corresponding difference diagrams are shown in Fig. 1.

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Table 1
Crystal data and structure refinement details for the RCu_3Te_3 (R = Er and Tm) compounds

Empirical formula	$ErCu_3Te_3$	$TmCu_3Te_3$
Space group	$Pmn2_1$ (no. 31)	$Pmn2_1$ (no. 31)
Unit cell dimensions	$a = 1.26784(6)$ nm	$a = 1.26756(3)$ nm
	$b = 0.76161(3)$ nm	$b = 0.76053(2)$ nm
	$c = 0.69016(3)$ nm	$c = 0.69034(2)$ nm
Volume	$0.66642(9)$ nm^3	$0.66550(5)$ nm^3
Number of formula units per unit cell	4	4
Calculated density	7.382 g/cm^3	7.408 g/cm^3
Absorption coefficient	139.970 mm^{-1}	141.399 mm^{-1}
$F(0\,0\,0)$	1244	1248
Diffractometer	Powder DRON-4-13	Powder DRON-4-13
2Θ range for data collection	10.00–100.00	10.00–100.00
Refinement method	Full profile	Full profile
R_I	0.0814	0.0639
R_P	0.1367	0.0900
Preferred orientation	[0 0 1]	[0 0 1]
Preferred orientation parameter	0.99(2)	1.10(1)

The atomic coordinates and the isotropic temperature factors are given in Table 2. Just one position of the R atoms, four positions of the Cu atoms and four positions of the Te atoms were established. A schematic view of the unit cell of $TmCu_3Te_3$ is presented in Fig. 2, together with the coordination polyhedra of the particular atoms. The Tm atoms have an octahedral surrounding, all the Cu atoms are located in tetrahedral environment, while all the Te atoms are surrounded by six atoms (4Cu + 2Tm).

The Te atoms are stacked in a close-packed arrangement with consecutive layers in the sequence *ABAB . . ..* The R atoms occupy one-third of octahedral interstices, whereas the Cu atoms occupy half of tetrahedral interstices. Fig. 3 shows the packing of the Tm-centered octahedra and Cu-centered tetrahedra in the crystal structure of $TmCu_3Te_3$.

The relevant interatomic distances and the coordination numbers of the atoms in the unit cells of both compounds are gathered in Table 3. Remarkably, all the interatomic distances are close to the sums of the respective ionic radii [4].
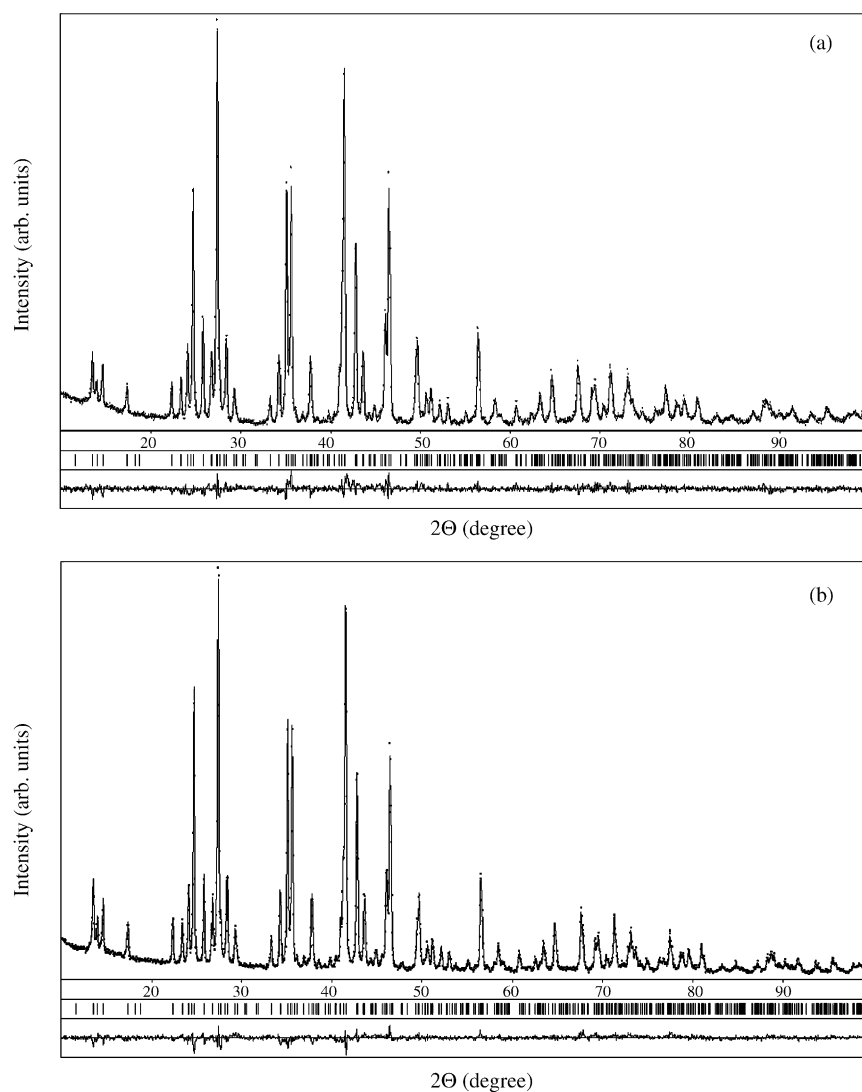

Fig. 1. The experimental and calculated diffractograms and the corresponding difference diagrams for $ErCu_3Te_3$ (a) and $TmCu_3Te_3$ (b).