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Change of magnetic properties of Th_2Fe_{17} due to interstitial solution of C and N

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The changes in magnetic and crystallographic properties in the series $Th_2Fe_{17}C_x$ and $Th_2Fe_{17}N_x$ have been studied. The changes in the latter series were also studied by ^{57}Fe Mössbauer spectroscopy. The ultimate enhancements of the saturation moments in these series are 13% and 24%, respectively. This is much larger than observed previously in the corresponding rare-earth compounds, although the Curie temperature enhancements are of comparable magnitude. In the Th–Fe–C system a novel compound of the $BaCd_{11}$ type was found, having a Curie temperature around 370 K.

I. INTRODUCTION

Interstitial solutions of C and N in rare-earth compounds of the type R_2Fe_{17} are prominent examples of how the magnetic properties of materials can be changed drastically without major changes of their crystal structure.[1,2] The compounds $R_2Fe_{17}C_x$ and $R_2Fe_{17}N_x$ are of interest partially due to the fact that the incorporation of C and N atoms significantly increases the Curie temperature and magnetic anisotropy, making them useful starting materials for permanent magnets. At the same time, there is substantial interest in these compounds from the fundamental physics side, making it possible to describe the observed changes in magnetic properties from basic principles. In the present investigation we have extended our study of the properties of interstitial compounds to include $Th_2Fe_{17}C_x$ and $Th_2Fe_{17}N_x$ in which the changes in Curie temperature and moment are as large as or even larger than in the corresponding rare-earth compounds.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The $Th_2Fe_{17}C_x$ compounds were made by arc melting, using materials of at least 99.9% purity. After melting, the samples were wrapped in tantalum foil and sealed in evacuated quartz tubes. The samples were annealed at 1100 °C for about two weeks and then quenched in water to room temperature. To prepare the $Th_2Fe_{17}N_x$ compound, we used powder of the compound Th_2Fe_{17} that had been prepared in the manner outlined above. The powder was heated in an atmosphere of N_2 gas at 500 °C for about 3 h.

All the samples were investigated by x-ray diffraction using Cu K_α radiation on a Philips x-ray diffractometer PW 1800, equipped with a single-crystal graphite monochromator. The results showed that the samples were single-phase, of the rhombohedral Th_2Zn_{17} structure type, up to a carbon concentration of $x=1.2$. In contrast to results obtained for most of the $R_2Fe_{17}C_x$ compounds, no free iron was observed in the diagrams.[1] However, for $x>1.2$, a second phase showed up in amounts exceeding the rhombohedral Th_2Zn_{17} phase for increasing carbon concentration. Eventually, for $x=3$, the x-ray diagram was found to contain almost exclusively this second phase. The $BaCd_{11}$ structure was tentatively assigned to this novel phase, having the space group $I4_1/amd$ with four formula units per cell. The x-ray diagram of $Th_2Fe_{17}N_x$ was completely single-phase, leading to the conclusion that the nitriding process had reached completion.

The lattice constants of all the samples derived from the x-ray diagrams are listed in Table I, including those of the $BaCd_{11}$ phase. We see an increase of the lattice parameters with increasing carbon concentration up to $x=1.5$. The addition of more carbon only leads to the formation of the $BaCd_{11}$ phase, which has almost the same lattice parameters for all nominal values of x. The $Th_2Fe_{17}N_x$ sample has a very large unit cell, and no $BaCd_{11}$ or other second phase was observed in its x-ray diagram.

The temperature dependence of the magnetization was measured by means of a Quantum Design superconducting quantum interference device (SQUID) magnetometer (5 $\text{K} \leqslant T \leqslant 350$ K) and by means of an automatic σ–T recorder based on the Faraday method (200 $\text{K} \leqslant T \leqslant 1000$ K), using polycrystalline powder samples. The Curie temperatures were determined from measurements of $\sigma(T)$ in low magnetic fields ($H \approx 40$ kA/m) by extrapolating $\sigma^2(T)$ to zero.

In Table I we have listed the magnetic ordering temperatures for all the compounds. Their values increase with x, as do the unit-cell volumes that may be derived from the lattice constants listed. The maximum value of T_c is about 480 K, saturating at $x=1.5$, after which concentration the contributions of the second phase start to grow, characterized by a Curie temperature of about 370 K. The

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TABLE I. Lattice parameters, Curie temperature and saturation magnetization of the $Th_2Fe_{17}C_x$ compounds, including those of $Th_2Fe_{17}N_x$ and of the $BaCd_{11}$ phase (if present). The saturation magnetization was measured at 5 K.

x	a (pm)	c (pm)	V (nm^3)	T_c (K)	M_s (Am^2/kg)	a (pm)	c (pm)	T_c (K)
		[$Th_2Fe_{17}C_x$]					[$BaCd_{11}$]	
0	857.3	1247.2	0.794	320	120			
0.3	860.2	1248.5	0.800	343	120			
0.6	863.7	1249.5	0.807	396	125			
0.9	866.3	1250.0	0.812	418	127			
1.2	869.4	1250.9	0.819	462	135			
1.5	871.2	1250.9	0.822	482	133			
1.6	871.5	1251.3		477				≃360
1.8	871.4	1251.0		477		1015.5	658.9	≃360
2.0	871.3	1252.9		472		1015.2	658.7	≃360
2.3	871.9	1252.7		485		1014.5	658.1	370
2.6				485		1013.9	657.7	359
3.0						1016.7	659.4	396
		[$Th_2Fe_{17}N_x$]						
2.6	879.8	1270.3	0.852	747	146			

$Th_2Fe_{17}N_x$ compound has a very high Curie temperature of about 750 K. It proved necessary to seal these powdered samples into small glass vials during the magnetic measurement, since otherwise oxidation or decomposition would have taken place.

The saturation magnetization was also measured by means of a Quantum Design SQUID magnetometer at 5 K in fields up to about 4400 kA/m (5.5 T). The values obtained for all the samples are listed again in Table I, as well as the corresponding magnetic moments of the iron atoms. Because Th is nonmagnetic, we have been able to determine the change of the magnetic moment of the iron atoms after nitrogenation, which is about 24%.

The ^{57}Fe Mössbauer spectra of Th_2Fe_{17} and its ternary nitride were measured on a constant acceleration Harwell spectrometer which utilized a Rh-matrix ^{57}Co source and was calibrated at room temperature with natural α–Fe foil. The hyperfine fields obtained from fitting the 78-K spectra are listed in Table II. A more detailed account of the Mössbauer measurements will be presented in a separate paper.

TABLE II. ^{57}Fe hyperfine fields derived from fits of the 78-K Mössbauer spectra for the various Fe sites in Th_2Fe_{17} and its ternary nitride (in Tesla).

Site	Th_2Fe_{17}	$Th_2Fe_{17}N_{2.6}$
6*c*	31.3	35.8
9*d*	22.5	30.3
18*f* (6)	27.7	38.4
18*f* (12)	26.2	34.7
18*h* (6)	24.9	31.7
18*h* (12)	23.0	33.1
average	25.4	33.8

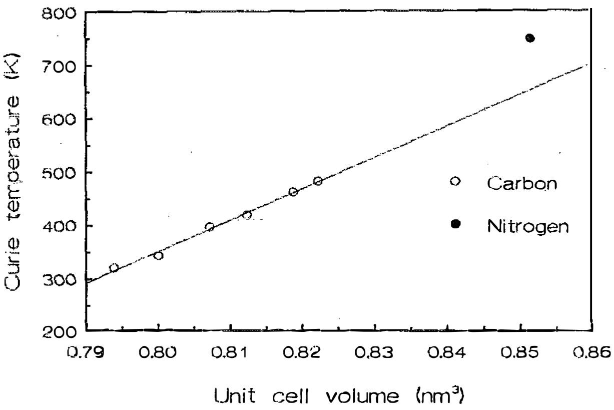

FIG. 1. Dependence of the Curie temperature on the unit-cell volume in samples of the composition $Th_2Fe_{17}C_x$ (○) and $Th_2Fe_{17}N_x$ (●).

III. DISCUSSION

We have observed a large increase of the unit-cell volume as well as of the Curie temperature, with increasing carbon concentration. Beyond a certain value of x ($x \simeq 1.5$) a kind of saturation occurs, both in the lattice parameters and in T_c. In Fig. 1 we have plotted the T_c data versus the corresponding unit-cell volume. We see a linear relation between the two quantities. From the observed relation we have calculated the value $\gamma = d\ln T_c/d\ln V$ for this series of compounds and obtained $\gamma = 15$. This value may be compared with the γ value obtained from pressure measurements performed by Brouha *et al.*[3] These authors obtained $\gamma = 13$ for Th_2Fe_{17}, meaning that we can explain the increase of T_c in $Th_2Fe_{17}C_x$ mainly by magneto volume effects. A similar result had already been reported by us for the carbides and nitrides of the R_2Fe_{17} compounds.[4,5]

Th_2Fe_{17} is a suitable compound for studying the effect of interstitials like carbon and nitrogen on the Fe moments. Th is, like the rare-earth element Ce, not trivalent but tetravalent and has an empty 5*f* shell and thus a zero magnetic moment. The saturation magnetization is completely due to the iron sublattice. For the pure Th_2Fe_{17} compound we found $M_s = 120$ Am^2/kg, which agrees with 30.4 $\mu_B/f.u.$ From the latter value we find an iron moment of 1.79 μ_B. This is in close agreement with results reported earlier.[6]

Inspection of the M_s values listed for $Th_2Fe_{17}C_x$ shows that they have a tendency to increase up to about $x = 1.5$. For higher concentrations the M_s values are representative of two-phase samples and will be left out of consideration here. It can be seen from the table that the values of M_s in $Th_2Fe_{17}C_{1.5}$ and $Th_2Fe_{17}N_x$ correspond to Fe moments of 2.03 and 2.22 μ_B, respectively. These Fe moments have nearly the same value as found in the ternary carbides and nitrides of the type $R_2Fe_{17}(C,N)_x$ (R = Y or Lu), respectively. Compared to Th_2Fe_{17}, the Fe moments in $Th_2Fe_{17}C_{1.5}$ and $Th_2Fe_{17}N_x$ have increased due to the interstitial hole filling by about 13% and 24%, respectively. These increases are much larger than those found in interstitial solutions of C and N in rare-earth compounds of the type R_2Fe_{17}. In the ternary rare-earth carbides the increase

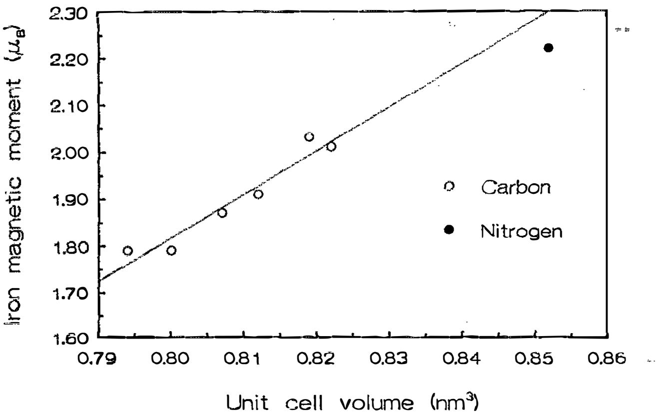

FIG. 2. Dependence of the Fe moment on the unit-cell volume in samples of the composition $Th_2Fe_{17}C_x$ (○) and $Th_2Fe_{17}N_x$ (●).

of the Fe moments is almost negligible, while in $R_2Fe_{17}N_x$ it reaches only about 10%.[7,8] We come therefore to the surprising conclusion that the moment enhancements due to interstitial solutions of C and N are much larger in Th_2Fe_{17} than in Y_2Fe_{17}.

A second surprising feature is that the T_c value of $Th_2Fe_{17}N_x$ is not located on the extrapolated volume dependence of T_c of the ternary carbides (see Fig. 1). In this respect the Th compounds differ from the rare-earth compounds, where the T_c values of $R_2Fe_{17}N_x$ (R = Y, Sm, Gd, Er, Tm) are located on the same T_c vs. V line as the T_c values of the corresponding $R_2Fe_{17}C_x$ compounds.[5,9] The comparatively strong T_c enhancement in $Th_2Fe_{17}N_x$ is not accompanied by an equally strong enhancement of the Fe moment. This may be illustrated in Fig. 2, where the Fe moments in $Th_2Fe_{17}C_x$ and $Th_2Fe_{17}N_x$ are plotted versus the corresponding unit-cell volume. In contrast to the data shown in Fig. 1, one sees in Fig. 2 that the Fe moment in the ternary nitride falls somewhat below the value obtained when extrapolating the $Th_2Fe_{17}C_x$ data to higher unit-cell volumes.

It is interesting to compare these results with band-structure calculations performed recently by Beuerle *et al.*[10] These authors simulated the effect of interstitial atom solution in Y_2Fe_{17} by artificially increasing the unit-cell volume of this compound. It follows from their calculations that the volume increase entails a moment increase of 10% in $Y_2Fe_{17}N_x$. This is indeed of the correct order of magnitude. The much stronger moment enhancement found by us in the interstitial compounds of Th_2Fe_{17} show that the situation is different from that in Y_2Fe_{17}, although the predicted trend is the same. It may be inferred from the hyperfine field data listed in Table II that the largest increases in moment are found for the Fe atoms located on the 18f and 18h positions while the moment increase of the so-called dumbbell Fe atoms (6c) is only modest. The average hyperfine fields in Th_2Fe_{17} and $Th_2Fe_{17}N_{2.6}$ when using a conversion factor of 14.8 T/μ_B correspond to average Fe moments of 1.71 μ_B and 2.28 μ_B, respectively. These values are in good agreement with the moment values derived from the magnetic measurements (Fig. 2).

Finally we wish to discuss the observation of a novel $BaCd_{11}$-structure-type phase occurring in the three-component system Th-Fe-C. To our knowledge this phase has not been observed before. Le Roy *et al.*[11] showed that in rare-earth-based materials, small amounts of Si are required to stabilize this structure, leading to compounds with the composition $RFe_{10}SiC_{0.5}$ (R = Ce, Pr, Nd, Sm). These compounds are isotypic with $LaMn_{11}C_{2-x}$ found by Jeitschko *et al.*[12] Carbon atoms fill octahedral voids formed by four manganese and two lanthanum atoms, site 8(c), leading to the maximum of two carbon atoms per formula unit. The occupancy of these sites is about 75% in $LaMn_{11}C_{2-x}$, corresponding to the formula $LaMn_{11}C_{1.52}$. In the $RFe_{10}SiC_{0.5}$ compounds the carbon atoms also occupy the 8(c) site, but with an occupancy of only 25%. The Curie temperatures of $RFe_{10}SiC_{0.5}$ lie between 390 and 460 K, which is close to the value found by us for the $BaCd_{11}$-type phase. We are currently engaged in determining the correct stoichiometry of $ThFe_{11}C_x$ in order to determine its crystal structure and its magnetic properties.

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