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Crystal Growth and Structure of Ho_2Fe_{17} and Ho_2Co_{17}

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Single crystals of the rare earth transition metal alloys Dy_2Co_{17}, Ho_2Co_{17}, Dy_2Fe_{17}, Ho_2Fe_{17}, Er_2Fe_{17}, Tm_2Fe_{17} and $ErFe_2$ were grown from cold crucibles using the Czochralski method or were grown in crucibles of BN by the Bridgman method.

The structure of Ho_2Fe_{17} was investigated by single crystal X-ray diffractometry and that of Ho_2Co_{17} by single crystal neutron diffractometry. Ho_2Fe_{17} is hexagonal, the space group is $P6_3/mmc$ (No. 194) with $a=8.458(5)$, $c=8.282(5)$ Å, $Z=2$. Ho_2Co_{17} is hexagonal with space group $P6_3/mmc$ (No. 194) with $a=8.322(6)$, $c=8.113(7)$ Å, $Z=2$. The two structures are partly disordered.

In connection with an investigation of magnetic excitation in single crystals of rare earth transition metal alloys[1] single crystals of the compounds R_2M_{17} have been made (R: Dy and Ho, M: Co and Fe).[2] Single crystals were also made of Er_2Fe_{17}, Tm_2Fe_{17} and $ErFe_2$. These compounds are ferri- or ferromagnetic and have been extensively studied due to their magnetic properties. The intermetallic compounds R_2M_{17} (R = rare earth, M = Fe, Co) have a hexagonal structure.[3] An investigation of the crystal structure of Lu_2Fe_{17}, showed that the alloy can exist in the composition range $LuFe_{8.5-9.5}$ and that the crystal structure is disordered with the degree of disorder dependent upon the method of preparation.[4] To understand the magnetic properties of the R_2M_{17} alloys it is thus necessary to make structure determinations of the specimens to determine the degree of disorder.

EXPERIMENTAL

Crystal Preparation. Single crystals of the alloys were obtained by Czochralski growth in a cold crucible or Bridgman growth in a BN crucible. The experimental conditions are listed in Table 1. Single crystals with volumes up to 1 cm^3 were obtained. The compounds were made from mixtures with an excess of up to 2 % of the rare earth metal.

Table 1. Growth conditions and unit cell parameters for some rare earth transition metal compounds.

Compound	Growth method[a]	He-gas pressure MPa	Growth rate mm h^{-1}	Length of crystal mm	Seed	Density g cm^{-3}	Unit cell parameters (Å) a	c
Dy_2Co_{17}	C	1.0	4	50	none	8.925	8.347(4)	8.129(2)
Ho_2Co_{17}	C	0.6	10	45	Ho_2Co_{17}	8.97	8.322(6)	8.113(7)
Dy_2Fe_{17}	C	1.0	3	10	none	8.356	8.473(5)	8.284(4)
Ho_2Fe_{17}	C	1.6	8	32	none	8.264	8.458(5)	8.282(5)
Er_2Fe_{17}	C	1.1	2	25	none	8.311	8.441(3)	8.280(8)
	B	1.4	2	25	none			
Tm_2Fe_{17}	C	1.7	2	20	none	8.292	8.412(2)	8.278(2)
	B	1.4	2	25	none			
$ErFe_2$	C	1.0	10	40	none		7.288(2)	

[a] C, Czochralski growth in cold crucible; B, Bridgman growth in BN crucible.

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The unit cell parameters of samples of the single crystals were obtained from Guinier powder patterns with germanium $a_{Ge}=5.6576$ Å as an internal standard. The growth directions and the quality of the crystals were investigated using Laue back reflection methods. The crystals were not annealed for long periods of time but were used as grown for the physical and crystallographic experiments.

X-Ray diffraction, Ho_2Fe_{17}. A single crystal of Ho_2Fe_{17} was investigated using monochromatic Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) and an automatic diffractometer with equiinclination Weissenberg geometry. A ϕ-scan technique was used in the investigation of the intensities that were measured with a scintillation counter. The single crystal had a volume of 3×10^{-6} cm^3 and linear dimensions up to 3×10^{-2} cm and was aligned along [010]. The crystal had a rather irregular shape and its surface could be described by five planes with the following Miller indices: (0 0 −1), (12 −7 4), (3 3 4), (−1 1 0), (−3 −9 5). 13 748 reflections were measured at $\sin\theta/\lambda<1.09$. After correction for absorption, $\mu_{(calc)}=394$ cm^{-1}, and data reduction a total of 528 independent reflections with $I>3\sigma(I)$ was obtained.

Neutron diffraction, Ho_2Co_{17}. A single crystal of Ho_2Co_{17} with a volume of 20 mm^3 and shaped as a cylinder was cut from a larger specimen using spark erosion technique. The crystal was mounted parallel to the cylinder axis that was close to the [001] direction. Neutron diffraction data were measured at 300 K on a four-circle diffractometer at DR3, Risø, using 1.07 Å neutrons. The measured reflections were selected to give an even distribution in reciprocal space covering 1/4 of a sphere and were selected after a structure factor calculation using the results of the X-ray structure determination of Ho_2Fe_{17}. After absorption correction with $\mu_{(calc)}=1.83$ cm^{-1}, and averaging of symmetry related reflections, the number of reflections with $I>3\sigma(I)$ was 79. At 300 K the compound is magnetically ordered and the reflections (0 3 0), (0 3 2), (1 1 0), (1 1 2), (1 4 0), (1 4 2), (2 2 0), (2 2 2), (3 3 0) and (3 3 2) that contain magnetic scattering contributions were rejected, leaving 69 reflections for the refinement.

Magnetic properties. The magnetic susceptibility was measured for Dy_2Fe_{17}, Ho_2Fe_{17}, Er_2Fe_{17} and Tm_2Fe_{17} in the temperature range 75−300 K using the Faraday method. All four compounds

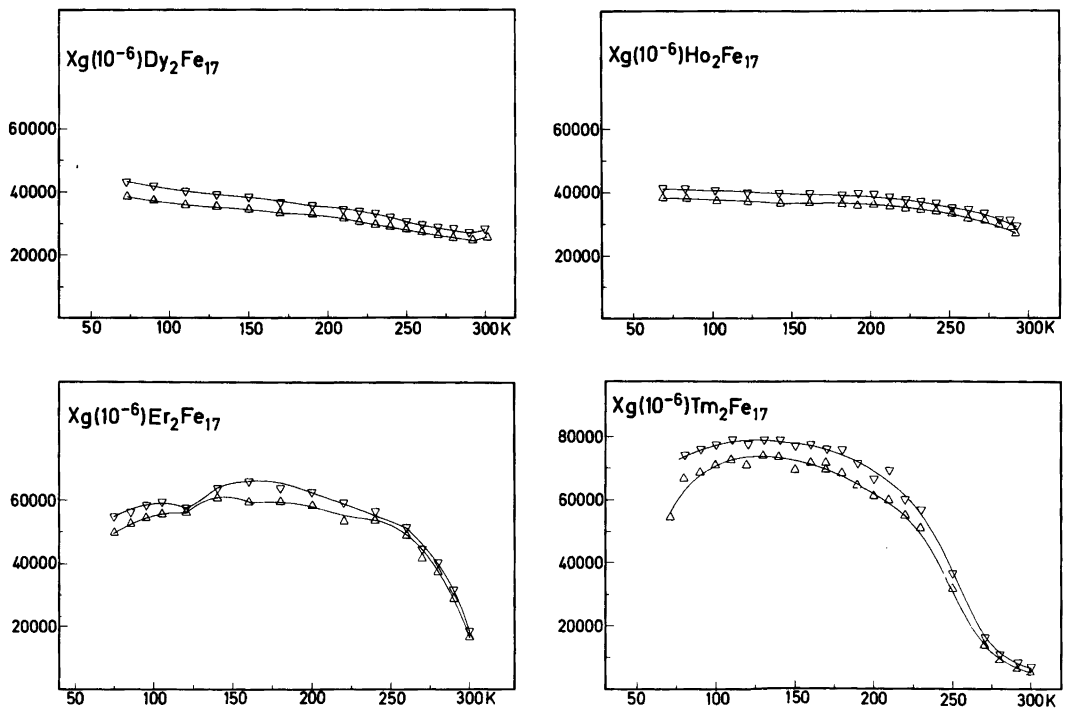

Fig. 1. The susceptibility χ_g *versus* the temperature for Dy_2Fe_{17}, Ho_2Fe_{17}, Er_2Fe_{17} and Tm_2Fe_{17}. All four compounds show hysteresis. Triangles with a corner up indicate magnetization and with a corner down demagnetization.

show a strong field dependence of χ_g in the temperature range (see Fig. 1) and hysteresis, χ_g being larger in demagnetization than in magnetization of the specimens. The following magnetic transition temperatures have been reported previously: Dy_2Fe_{17}: 364 K, Ho_2Fe_{17}: 335 K, Er_2Fe_{17}: 297 K, Tm_2Fe_{17}: 275 K,[5] and the results obtained in the present measurements are not in conflict with these previous values.

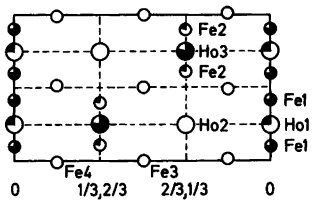

Fig. 2. Packing of the atoms in the diagonal plane of the unit cell of Ho_2Fe_{17}. The black area of the circles indicates the fraction of the atoms that is statistically missing.

STRUCTURES AND DISCUSSIONS

Ho_2Fe_{17}. The X-ray data were used in a least-squares programme (LINUS)[6] to refine the structure. As a starting model for the structure was taken that of Ho_2Co_{17} described by Bouchet *et al.*[3] that has the Co-atoms in the sites 6*g*, 12*j*, 12*k* and 4*f*, and the Ho-atoms in the sites 2*b* and 2*d* of the space group $P6_3/mmc$ (No. 194). A series of structure factor calculations using the atomic scattering factors reported by Cromer and Mann,[7] corrected for anomalous dispersion,[8] and Fourier calculations showed additional electron density at the sites 4*e* and 2*c* with $z=0.11$ and $z=0.25$, respectively. When a holmium atom with a smaller occupancy than the theoretically possible was inserted in site 2*c* and similarly an iron atom in site 4*e* the structure refined to a conventional *R*-value of 8.9 %. In the last refinements the occupancy parameters were not refined for the atoms Ho2, Fe3 and Fe4, the sites of these three atoms were found to be occupied fully.

The disorder is caused by the holmium atom Ho1 sometimes being replaced by a pair of iron atoms, Fe1, or by a pair of Fe2 atoms being replaced by one Ho3 atom (see Fig. 2 that shows a section along the long diagonal of the unit cell). This limits the occupation factors σ of these atoms. The Fe5 position is so close to Ho3 that they can probably not be occupied at the same time. In Lu_2Fe_{17} the corresponding iron atom is found to be disordered but this seems to be impossible with the larger holmium atom, although the thermal parameters indicate larger displacements in the *ab*-plane than in the *c*-direction. The thermal parameters for Fe4 hint a possible disorder along *c*, but refinement showed the splitting to be insignificant. Refinements showed that the constraints $\sigma(Fe1)+2\sigma(Ho1)=1/6$, $\sigma(Fe2)+2\sigma(Ho3)=1/6$ and $\sigma(Fe5)+6\sigma(Ho3)=1/2$ gave the best agreement. Further constraints employed were $z(Fe1)=z(Fe2)$ and throughout the temperature factors for the Ho(3) and Fe(1) were kept at the value of the overall isotropic temperature factor. The final refinements with anisotropic thermal parameters for the other atoms included 27 parameters and gave the results listed in Table 2. The isotropic extinction correction was severe with about 50 % transmission for 004 and 220. The composition from the X-ray analysis is $Ho_{2.0(1)}Fe_{15.9(3)}$.

Table 2. Results of the X-ray structure determination of Ho_2Fe_{17}. $R=8.9$ %.[a]

Atom	Site	Occupancy Theory	Found	%	*x*	*y*	*z*	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ho1	2*b*	0.08333	0.064(1)	77	0	0	1/4	84(5)	84	147(17)	42	0	0
Ho2	2*d*	0.08333	0.08333	100	1/3	2/3	3/4	64(2)	64	87(7)	32	0	0
Ho3	2*c*	0.08333	0.0168	20	1/3	2/3	1/4	74					
Fe1	4*e*	0.16667	0.039	23	0	0	0.107	74					
Fe2	4*f*	0.16667	0.1331(4)	80	1/3	2/3	0.1068(6)	81(5)	81	48(13)	40	0	0
Fe3	6*g*	0.25	0.25	100	1/2	0	0	64(31)	81(19)	129(16)	40	−19	−38(22)
Fe4	12*k*	0.50	0.50	100	0.1669	0.3337(6)	0.9862(3)	77(17)	80(10)	105(8)	40	−22	−44(28)
Fe5	12*j*	0.50	0.3994	80	0.3289(6)	0.9588(5)	1/4	65(9)	74(12)	40(7)	−4(7)	0	0

[a] Isotropic extinction parameter: 0.29(4). The temperature factor parameters are multiplied by 10^4. A list of observed and calculated structure factors is available on request.

Table 3. Results of the neutron diffraction structure determination of Ho_2Co_{17}. $R = 5.8$ %.[a]

Atom	Site	Occupancy Theory	Found	%	x	y	z	B(Å²)
Ho1	2b	0.08333	0.082(8)	98	0	0	1/4	0.55
Ho2	2d	0.08333	0.08333	100	1/3	2/3	3/4	0.55
Ho3	2c	0.08333	0.015	18	1/3	2/3	1/4	0.55
Co2	4f	0.16667	0.136(2)	82	1/3	2/3	0.101(2)	0.55
Co3	6g	0.25	0.25	100	1/2	0	0	0.55
Co41	12k	0.5	0.408	82	0.165	0.330(3)	0.968(1)	0.55
Co42	12k	0.5	0.092	18	0.165	0.330	1.032	0.55
Co5	12j	0.5	0.408	82	0.330(3)	0.956(2)	1/4	0.55

[a] A list of observed and calculated structure factors is available on request.

The calculated density 7.9(2) g cm^{-3} is within two standard deviations in agreement with the measured density 8.28 g cm^{-3} determined by the method of Archimedes. The absorption of the compound is rather high ($\mu = 394$ cm^{-1}) and the relatively high value for the *R*-factor, 8.9 %, should be considered in that relation.

Ho_2Co_{17}. As starting parameters in the structure factor calculations were used the results obtained from the X-ray structure determination of Ho_2Fe_{17}. The scattering lengths used were 0.85 and 0.28 (in units of 10^{-12} cm) for Ho and Co.[9] Fourier maps and least-squares refinement gave the results listed in Table 3. The cobalt atom corresponding to the iron atom Fe1 in the structure described above is missing, and the cobalt atom Co4 is split in two positions. The occupancies of the atoms were constrained in the following way: $\sigma(\text{Ho3}) + 0.5\,\sigma(\text{Co2}) = 1/12$, $\sigma(\text{Co5}) + 6\sigma(\text{Ho3}) = 1/2$, $\sigma(\text{Co42}) + \sigma(\text{Co41}) = 1/2$ and $\sigma(\text{Co41}) = \sigma(\text{Co5})$. The only occupancy factors refined were thus those of Ho1 and Co2. In addition, the scale factor, the positional parameters and an over-all isotropic temperature factor parameter were refined. The parameters were determined with rather large standard deviations due to the limited number of observations. The composition from the neutron diffraction analysis is $Ho_{2.1(2)}Co_{16(1)}$. The calculated density is 8.8(6) g cm^{-3} in acceptable agreement with the measured density 8.97 g cm^{-3}. The investigation shows that Ho_2Co_{17} has a disordered structure of the same nature as found for Lu_2Fe_{17} and Ho_2Fe_{17}. Fig. 3 shows the diagonal plane of the unit cell.

The three compounds Lu_2Fe_{17}, Ho_2Fe_{17} and Ho_2Co_{17} have the same type of structure and all of them show deviation from the stoichiometric composition and disorder in the crystals investigated. The four crystals (two from the investigation of Lu_2Fe_{17}) show significant differences in the occupancies of the atomic sites. A structure determination of the crystal specimens used for investigation of the magnetic properties is therefore a help to obtain a detailed understanding of the magnetic properties.

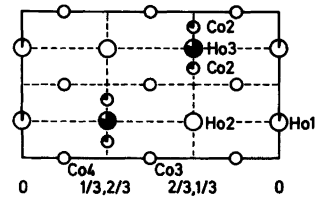

Fig. 3. Packing of the atoms in the diagonal plane of the unit cell of Ho_2Co_{17}. The black area of the circles indicates the fraction of the atoms that is statistically missing.

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