MISSOURI S&T

Missouri University of Science and Technology

Scholars' Mine

Chemistry Faculty Research & Creative Works

Chemistry

01 Jan 1984

Magnetic and Crystallographic Structure of Y₆Mn₂₃D₂₃

K. A. Hardman-Rhyne

James J. Rhyne

E. Prince

Cyrus E. Crowder

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/1613

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

Part of the Chemistry Commons

Recommended Citation

Magnetic and crystallographic structure of $Y_6Mn_{23}D_{23}$

Kay Hardman-Rhyne, J. J. Rhyne, and E. Prince

National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234

C. Crowder* and W. J. James

Graduate Center for Materials Research, University of Missouri—Rolla, Rolla, Missouri 65401

(Received 6 June 1983)

The magnetic behavior of Y_6Mn_{23} is dramatically altered upon hydrogenation (or deuteration). In this study it has been found, by means of high-resolution powder diffraction and Rietveld refinement techniques, that the crystallographic structure is distorted from face-centered cubic ($Fm3m$) at 295 K to a primitive tetragonal structure at 4 K in which deuterium atoms are atomically ordered. Y_6Mn_{23} is a ferromagnetic compound with $T_c = 486$ K, and bulk magnetization of $13.2\mu_B$/f.u. (formula unit). After deuteration of Y_6Mn_{23} to the composition $Y_6Mn_{23}D_{23}$, low-temperature scattering data ($T < 180$ K) show that the b and f_2 sites in the $Fm3m$ structure are antiferromagnetic and the d and f_1 sites have no spontaneous magnetic moment.

INTRODUCTION

Y_6Mn_{23} is a face-centered-cubic (fcc) compound isostructural with Th_6Mn_{23}, which has the space group $Fm3m$. The magnetic and crystallographic properties of these materials are greatly altered by hydrogenation (deuteration). Th_6Mn_{23} is a Pauli paramagnet, while the deuteride $Th_6Mn_{23}D_{30}$ is almost ferromagnetic (one Mn spin coupled antiparallel to the other 22 parallel Mn spins), with $T_c = 355$ K, and a bulk magnetization value of $18.4\mu_B$/f.u. (formula unit).[1,2] In contrast, from bulk studies, $Y_6Mn_{23}D_{23}$ exhibits no net spontaneous magnetization,[3,4] while Y_6Mn_{23} is a ferromagnetic compound with $T_c = 486$ K and a bulk magnetization of $13.2\mu_B$/f.u.[5] The magnetic structure of Y_6Mn_{23} is collinear, with spins along the [111] direction with the b site (one Mn atom), and the d site (six Mn atoms) coupled antiparallel to the two f sites (eight Mn atoms each). All magnetically ordered spins within each of the sites are coupled in the same direction. The interatomic distances of the Mn atoms vary significantly between different sites which partly accounts for the wide variations of Mn magnetic moments observed in the magnetically ordered compounds of this class. The magnetic properties of these hydrides are also strongly affected by changes in the electronic band structure.[1]

$R_6Mn_{23}H_x$ compounds are of interest in developing models for predicting the potential occupancy and location of hydrogen in rare-earth intermetallic compounds.[6,7] These compounds are very complex (e.g., $Y_6Mn_{23}D_{23}$ has four formula units or 208 total atoms per unit cell). A geometric model developed by Westlake shows nine different sites are possible for the D atoms, but in many of the combinations not all the sites can be simultaneously occupied.[6]

Neutron diffraction has proven to be a valuable tool in understanding the magnetism and the deuterium occupancy and location in these compounds. In this paper we will discuss the changes occurring in both the crystallographic

structure and the magnetic ordering of $Y_6Mn_{23}D_{23}$ at low temperatures.

EXPERIMENTAL OBSERVATIONS

An ingot of Y_6Mn_{23} was prepared by induction melting of 99.9% pure elements in a water-cooled Cu boat under an argon atmosphere. X-ray diffraction photographs showed that the specimen was single phase. The ingot was deuterated with 99.5% pure deuterium in a stainless-steel vessel at 20 atm and 110 °C for 2 h. Pressure-volume measurements indicated approximately 23 atoms of deuterium absorbed per formula unit. Deuterium was used in lieu of hydrogen because hydrogen has a large incoherent scattering cross section for neutrons. Figure 1 shows a deuterium absorption isotherm for Y_6Mn_{23}, demonstrating
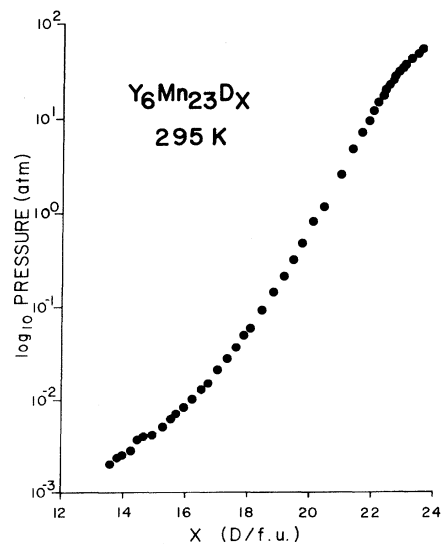

FIG. 1. Absorption isotherm for deuterium in Y_6Mn_{23}. Note that a plateau does not exist in this range (see Ref. 8).

TABLE I. Atomic parameters for $Y_6Mn_{23}D_{23}$ at 295 K in the fcc ($Fm\,3m$) structure. Refined occupancy is N (maximum occupancy of that site), position is (x,y,z), and B is the Debye-Waller temperature factor.

Atom	Site	$N/2$ f.u. (max)	x	y	z	B
Y	e	12 (12)	0.205	0	0	0.82
Mn	b	2 (2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.47
Mn	d	12 (12)	0	$\frac{1}{4}$	$\frac{1}{4}$	0.47
Mn	f_1	16 (16)	0.179	0.179	0.179	0.47
Mn	f_2	16 (16)	0.372	0.372	0.372	0.47
D	a	2 (2)	0	0	0	6.35
D	f_3	10 (16)	0.100	0.100	0.100	1.37
D	j_1	20 (48)	0	0.169	0.373	4.95
D	k_1	14 (48)	0.161	0.161	0.049	2.28

$$a_0 = 12.805 \text{ Å} \qquad R_{wp} = 10.64 \qquad X = 1.69$$
$$Z = 4 \qquad R_e = 6.29$$

the low pressures required to obtain deuteration up to 24 atoms per formula unit.[8] No absorption plateau is found in this region. This is in sharp contrast to $Th_6Mn_{23}D_x$,[2] which has a broad absorption plateau from 17 to 24 atoms of deuterium.

Neutron-diffraction data on pure and deuterated

Y_6Mn_{23} samples were taken at the National Bureau of Standards Reactor utilizing a high-resolution five-detector powder diffractometer. Neutrons of wavelength 1.542 Å were obtained from a (220) reflection copper monochromator, with a graphite filter to eliminate second-order contamination. Soller slit collimators of angular diver-
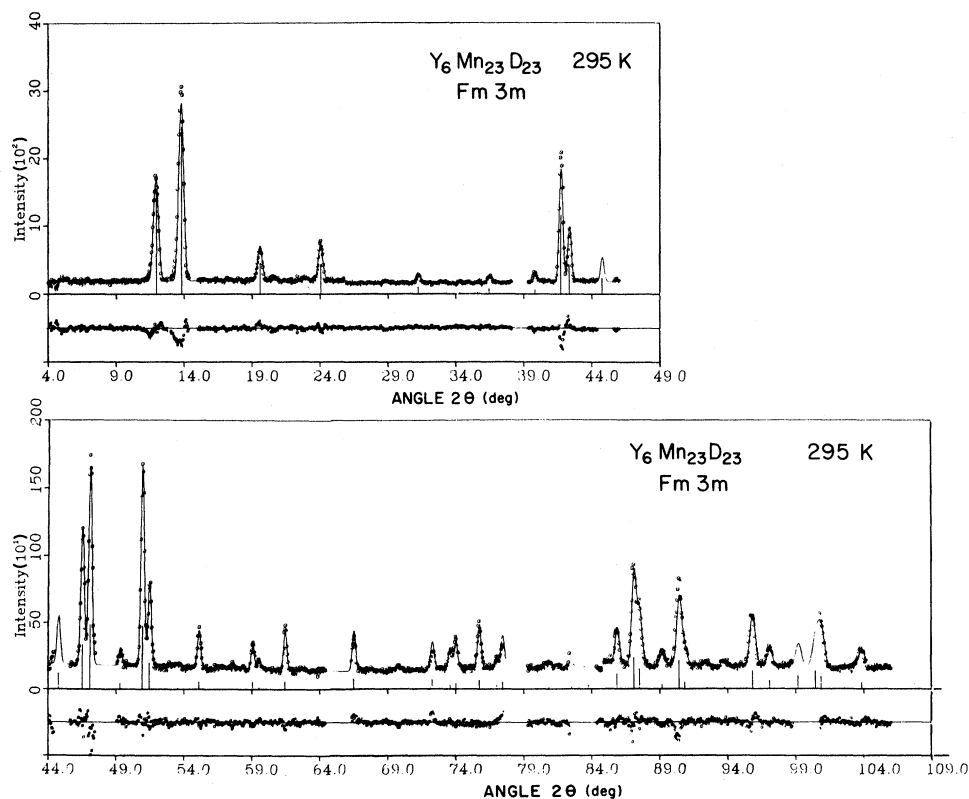

FIG. 2. Neutron-diffraction data on $Y_6Mn_{23}D_{23}$ at 295 K which is above the crystallographic phase transition and magnetic ordering temperature. The top half of the figure shows data and residuals from the first two of the five detectors (note the difference in scale of intensities). The solid curve is the calculated profile fit to the data and the vertical lines represent the calculated relative intensity and position of the nuclear reflections.

gences 10'-20'-10' were placed before and after the mono-chromator and in front of the detector, respectively.

The powder data from the five detectors, displaced in angle by 20° from each other, covered the 2θ range from 10° to 115° in increments of 0.05° and were analyzed by a modified Rietveld total pattern refinement technique which allowed background parameters to be refined in addition to the other structural and instrumental variables.[9] Standard deviations were generally less than ± 2 in the last digit listed, except for the magnetic moments which were $\pm 0.1\mu_B$/atom. The standard deviations of the thermal factors (B) for deuterium atoms in some cases were quite large (order of 30%).

RESULTS AND DISCUSSION

$Y_6Mn_{23}D_{23}$ at 295 K

At 295 K, $Y_6Mn_{23}D_{23}$ has no long-range magnetic ordering and is face-centered cubic, with space group $Fm3m(O_h^5)$. Although previous experiments have suggested that it has a body-centered-tetragonal (bct) structure with space group $I4/mmm(D_{4h}^{17})$,[4] the present studies conducted with higher-instrumental resolution and over a wider scattering angle range do not indicate a departure from the fcc symmetry. No peaks were found which could not be indexed on the $Fm3m$ cell, nor was there appreciable broadening or splitting of the peaks compared with the nondeuterated Y_6Mn_{23}. The structural parameters derived from the refinement are given in Table I. The

deuterium atoms are found to prefer occupying the a, f_3, j_1, and k_1 sites. These results are in basic agreement with Westlake's geometric model,[6] but in significantly less agreement with the heat of formation model of Jacob[7] which does not include the possibility of deuterium in a j_1 site. Both Jacob's and Westlake's models suggested the possibility of deuterium atoms located in the a, f_3, i, and j_2 sites. Westlake also considered the h and l sites in his model. Our results found no deuterium atoms in the i, h, j_2, or l sites.

Based on the geometric model[6] criteria that hydrogen atoms cannot be closer together than 2.1 Å, the j_1 site cannot have more than 12 deuterium atoms per formula unit or 48 deuterium atoms per unit cell. Our results (Table I) show ten D/f.u. present in the j_1 site. The model also predicts that D atoms cannot occupy the k_1 site unless some deuterium atoms are removed from the f_3 site. This was indeed found to be the case in this study of $Y_6Mn_{23}D_{23}$, in contrast to that of Commandre et al.[3] They reported the f_3 site filled (eight D/f.u.), and four D atoms in the k_1 site, whereas we have five D atoms in the f_3 site, and seven D atoms in the k_1 site per formula unit. On careful examination of the positions of the deuterium atoms in the f_3 and k_1 sites with the use of the Westlake geometric model, we expect that a maximum number of 20 deuterium atoms could exist in the k_1 site if no D atoms were present in the f_3 site. Furthermore, one deuterium atom removed from the f_3 site allows three D atoms to be added to the k_1 site. Thus if there are five D
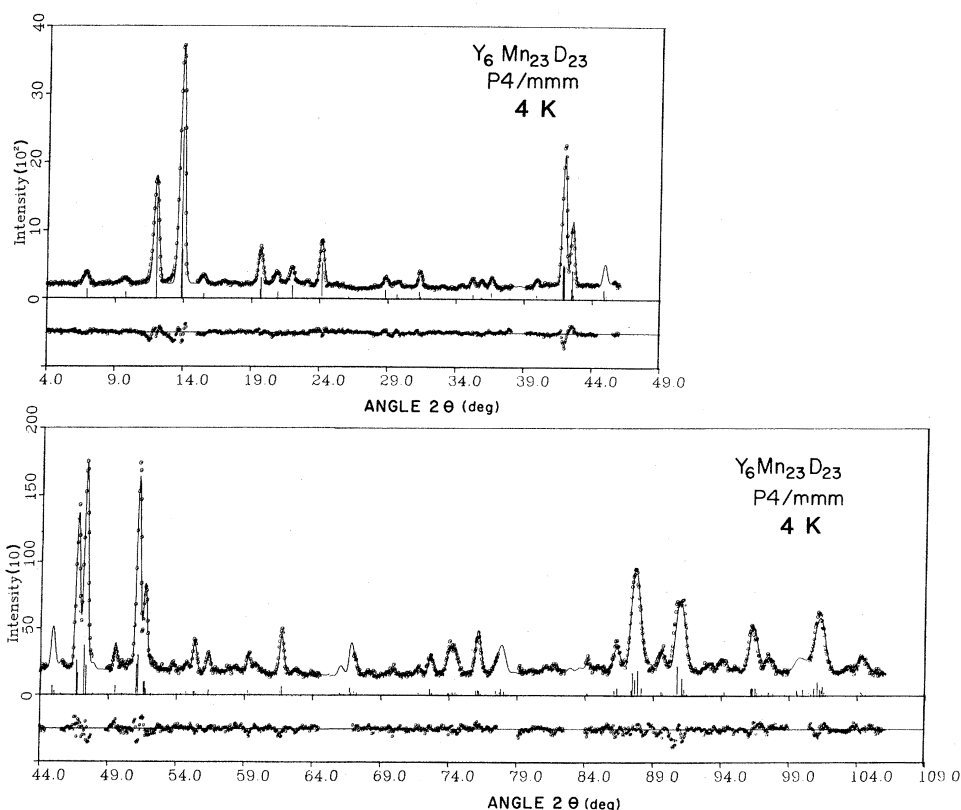

FIG. 3. Neutron-diffraction data and profile fit of $Y_6Mn_{23}D_{23}$ at 4 K. Additional peaks result from antiferromagnetism as well as the structural distortion, which is best fit by the primitive tetragonal space group $P4/mmm$.

atoms in the f_3 site, no more than nine D atoms can be present in the k_1 site. The composition $Y_6Mn_{23}D_{25}$, as found by Malik et al.,[1] could then be obtained by having one D atom in the a site, ten D atoms in the j_1 site, five D atoms in the f_3 site, and nine D atoms in the k_1 site; or by assigning twelve D atoms to the j_1 site, five D atoms to the f_3 site, and seven D atoms to the k_1 site. However, if more than 25 total D atoms are present [e.g., $Th_6Mn_{23}D_{30}$ (Ref. 2)] then more D atoms may occupy the k site.

The temperature factors B for deuterium in the a and j_1 sites are quite large. For deuterium located in the a site, the high thermal factor suggests little or no bonding of deuterium with the six Y atoms surrounding it. This volume is very large, and the deuterium atom is probably exhibiting large amplitude excursions. An alternate interpretation is that the a site is not actually occupied by the deuterium.[10] The high thermal factor for deuterium atoms in the j_1 site probably arises from an averaging effect of D atoms disordered between two j_1 sites that are only 0.90 Å from one another. The diffraction pattern, with the accompanying calculated profile fit, is shown in Fig. 2 for $Y_6Mn_{23}D_{23}$ at 295 K.

Crystallographic structure of $Y_6Mn_{23}D_{23}$ at 78 and 4 K

A crystallographic distortion is seen from the 4-K diffraction pattern in Fig. 3. A similar structural distortion was also found in $Th_6Mn_{23}D_{16}$ at 4 K (see Fig. 5 in Ref. 2). In the cases of $Th_6Mn_{23}D_{16}$ at 4 K and $Y_6Mn_{23}D_{23}$ at 78 and 4 K, the resulting structure is based on a primitive tetragonal cell. The lattice parameters of this cell are the same for $Y_6Mn_{23}D_{23}$ at 4 and 78 K, and are $a_0 = 9.030$ Å and $c_0 = 12.722$ Å, giving a ratio of c to $\sqrt{2}a$ of 0.996. The c_0 value obtained for $Y_6Mn_{23}D_{23}$ at 78 K from a fcc structure refinement is 12.766 Å. An enlargement of a limited high-angle range of the diffraction pattern at both 295 and 4 K, with the fcc profile fit applied to both, is shown in Fig. 4. The calculated curve at 4 K has been shifted to account for the decrease in the lattice parameter with temperature. In the 4-K data at $2\theta = 91.0°$, the (11,3,3) and (9,7,3) reflections have split and the intensities have changed. In the fcc lattice at 295 K there is only one peak in this region.

Of several possible space groups the one that provides the best fit to the nuclear structure of $Y_6Mn_{23}D_{23}$ at low temperatures ($T < 180$ K) is $P4/mmm(D_{4h}^1)$. As given in Table II, this structure splits the single Y e site into four sites (g, h, j, and k) and the Mn b site into b and c sites. The Mn d site is split into e, f, and r_1 sites. The Mn f site and the D f site are split into s and t sites. The D a site is split into a and d sites, and the j site is split into p, q, and four r sites. Only half of the original j site can be filled. Therefore the p and q sites cannot each be more than half-full, and only two r sites (or no more than half of all four r sites) can be filled. Our results, given in Table III, show that the p site is half-full, the q site is almost half-full, and the r_2 and r_4 sites are almost completely filled. There are no D atoms in the r_3 and r_5 sites. The k site splits into s_4, t_4, and two u sites. As mentioned before, no more than nine D atoms per formula unit can

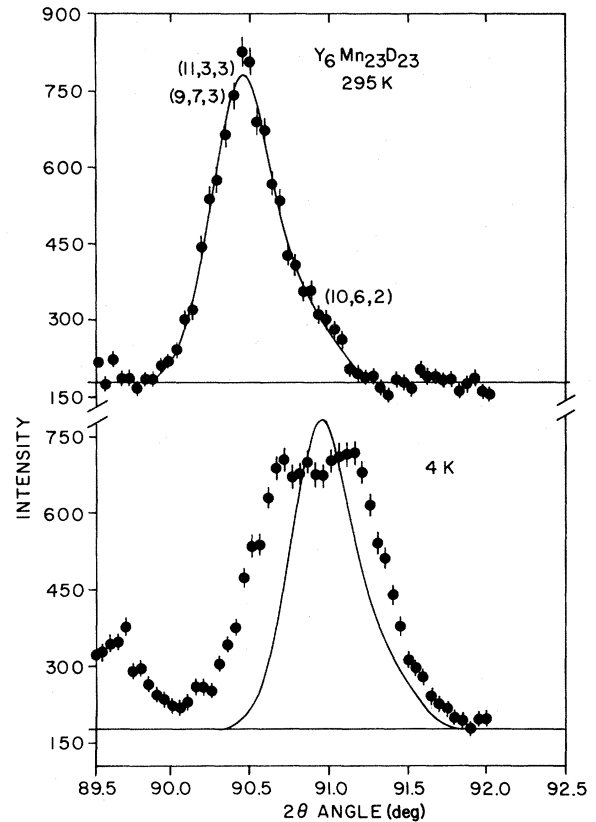FIG. 4. Expanded high-angle data for $Y_6Mn_{23}D_{23}$ at 295 and 4 K, showing the peak broadening accompanying the tetragonal distortion below the crystal-structure transition temperature. Solid lines in both cases are the profile fit for the 295 K fcc data. Shift in the solid line represents the lattice contraction that has occurred at low temperatures.
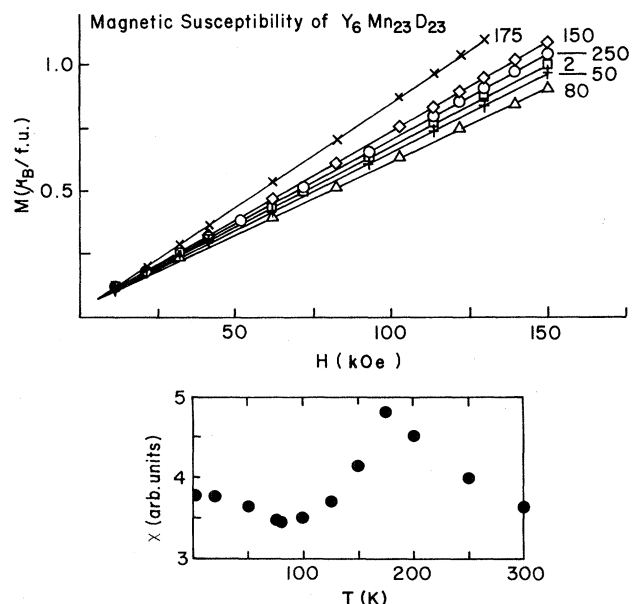

FIG. 5. Magnetic susceptibility for $Y_6Mn_{23}D_{23}$ (from Ref. 4).

fill these sites. Our results (Table III) show the t_4 site to be empty of D atoms. To illustrate the small distortion in the unit cell, the fcc equivalent positions are given for the tetragonal cell in Table II. Modest shifts in positions (x,y,z) can be seen from the fcc equivalent positions (Table III) for some sites. The crystal-structure transformation at low temperatures may result from preferential occupation by the D atoms among the many sites that are available. In particular, the fact that the r_3, r_5, and t_4 sites are empty of D atoms could lead to a crystallographic transition.

As previously mentioned, a bct structure with space group $I4/mmm$ has been suggested[4] for $Y_6Mn_{23}D_{23}$ at both room temperature and 78 K for the nuclear structure only. However, the present higher-resolution data at both 78 and 4 K show several structural details which clearly make the $P4/mmm$ symmetry the better choice. This includes several predominately nuclear peaks found at high angles (e.g., at 2θ about 56.3° and in the range 2θ from

69.4° to 69.9° and 84.9° to 85.6°) which are forbidden by the $I4/mmm$ symmetry but are allowed and well represented by the $P4/mmm$ structure. In addition, the unresolved asymmetric peak at 90.5° (Fig. 4) which arises from several reflections is fit considerably better by the composite structure factor of the primitive space group.

Magnetic structure of $Y_6Mn_{23}D_{23}$ at 78 and 4 K

Malik et al.,[1] Commandre et al.,[3] Buschow,[11] and Crowder et al.[4] have discussed the drastic reduction and ultimate disappearance of magnetization of Y_6Mn_{23} upon hydrogenation or deuteration. There has been much speculation on these effects, with suggestions of either a spin glass or an antiferromagnetic state in $Y_6Mn_{23}D_{23}$ and $Y_6Mn_{23}D_{25}$. A plot of the magnetic susceptibility of $Y_6Mn_{23}D_{23}$ versus temperature[12] in Fig. 5 shows a broad anomaly suggestive of a Néel temperature T_N, approxi-

TABLE II. Equivalent positions in two crystallographic space groups. $Z=4$ for the $Fm3m$ structure, and $Z=2$ for the $P4/mmm$ structure.

Face-centered cubic ($Fm3m$)				Primitive tetragonal ($P4/mmm$)					
atom	site	x,y,z	$N/2$ f.u.	site	x,y,z	x	y	z	$N/2$ f.u.
Y	e	$x,0,0$	12	g	$0,0,z$			0.205	2
		$x=0.205$		h	$\frac{1}{2},\frac{1}{2},z$			0.295	2
				j	$x,x,0$	0.205			4
				k	$x,x,\frac{1}{2}$	0.295			4
Mn	b	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	2	b	$0,0,\frac{1}{2}$				1
				c	$\frac{1}{2},\frac{1}{2},0$				1
Mn	d	$0,\frac{1}{4},\frac{1}{4}$	12	e	$0,\frac{1}{2},\frac{1}{2},$				2
				f	$0,\frac{1}{2},0$				2
				r_1	x,x,z	0.25		0.75	8
Mn	f_1	x,x,x	16	s_1	$x,0,z$	0.358		0.179	8
		$x=0.179$		t_1	$x,\frac{1}{2},z$	0.142		0.321	8
Mn	f_2	x,x,x	16	s_2	$x,0,z$	0.256		0.372	8
		$x=0.372$		t_2	$x,\frac{1}{2},z$	0.244		0.128	8
D	a	$0,0,0$	2	a	$0,0,0$				1
				d	$\frac{1}{2},\frac{1}{2},\frac{1}{2},$				1
D	f_3	x,x,x	16	s_3	$x,0,z$	0.200		0.100	8
		$x=0.100$		t_3	$x,\frac{1}{2},z$	0.300		0.400	8
D	j_1	$0,y,z$	48	p	$x,y,0$	0.204	0.458		8
		$y=0.169$		q	$x,y,\frac{1}{2}$	0.296	0.042		8
		$z=0.373$		r_2	x,x,z	0.127		0.331	8
				r_3	x,x,z	0.169		0.373	8
				r_4	x,x,z	0.331		0.127	8
				r_5	x,x,z	0.373		0.169	8
D	k_1	x,x,z	48	s_4	$x,0,z$	0.322		0.049	8
		$x=0.161$		t_4	$x,\frac{1}{2},z$	0.178		0.451	8
		$z=0.049$		u_1	x,y,z	0.112	0.210	0.161	16
				u_2	x,y,z	0.290	0.388	0.339	16

mately 170 K. This value is in good agreement with that found by Stewart et $al.$[13] ($T_N = 180$ K) by Mössbauer studies on $Y_6(^{57}Fe_{0.005}Mn_{0.995})_{23}H_{25}$. They found antiferromagnetic ordering of the Mn sites in this substituted compound.

Our neutron-diffraction measurements show new peaks emerging in the 2θ range from 20.0° to 21.5° at temperatures between 165 and 178 K. Analysis of the $Y_6Mn_{23}D_{23}$ data at 78 and 4 K reveals a weak antiferromagnetic structure with only two sites participating in the long-range order. The magnetic moments of the Mn atoms are given in Table IV, and involve only the b and f_2 sites of the original fcc structure. The Mn moments are along the c axis. The splitting of the f sites allows the Mn atoms to be divided among two sites (s and t) with antiparallel moments, which represents antiferromagnetism on the equivalent fcc site. Surprisingly, the d and f_1 sites of the fcc structure appear to have no magnetic moment. If any

magnetic moment is forced onto these sites they prefer to couple ferromagnetically. However, the best profile fits were those with no magnetic moments on the d and f_1 sites. Larger moments on the f_2 (really s_2 and t_2 in the $P4/mmm$ structure) sites were found for $Y_6Mn_{23}D_{23}$ at 78 K rather than at 4 K. This corresponds to the broad minimum observed around 80 K in the magnetic susceptibility (Fig. 5).

CONCLUSIONS

The deuterium occupancy and location has been determined for $Y_6Mn_{23}D_{23}$ at 295 K where the crystal structure is face-centered cubic with space group $Fm3m$. The deuterium atoms fill the a site and partially fill the $f_3, j_1,$ and k_1 sites, which is in relatively good agreement with the Westlake model for $A_6B_{23}H_x$ compounds.

There is a structural and accompanying magnetic tran-

TABLE III. Atomic parameters of $Y_6Mn_{23}D_{23}$ at 78 and 4 K in the $P4/mmm$ tetragonal structure. All $x,y,z,$ and B values were refined except the x,y,z values that are 0 or $\frac{1}{2}$. All deuterium occupancy values were also refined.

atom	site	N (max)	78 K				4 K			
			x	y	z	B	x	y	z	B
Y	g	2 (2)	0	0	0.208	0.76	0	0	0.213	0.72
	h	2 (2)	$\frac{1}{2}$	$\frac{1}{2}$	0.287	0.76	$\frac{1}{2}$	$\frac{1}{2}$	0.285	0.72
	j	4 (4)	0.199	0.199	0	0.76	0.204	0.204	0	0.72
	k	4 (4)	0.291	0.291	$\frac{1}{2}$	0.76	0.297	0.297	$\frac{1}{2}$	0.72
Mn	b	1 (1)	0	0	$\frac{1}{2}$	0.25	0	0	$\frac{1}{2}$	0.01
	c	1 (1)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.25	$\frac{1}{2}$	$\frac{1}{2}$	0	0.01
Mn	e	2 (2)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.25	0	$\frac{1}{2}$	$\frac{1}{2}$	0.01
	f	2 (2)	0	$\frac{1}{2}$	0	0.25	0	$\frac{1}{2}$	0	0.01
	r_1	8 (8)	0.259	0.259	0.748	0.25	0.255	0.255	0.747	0.01
Mn	s_1	8 (8)	0.360	0	0.177	0.25	0.360	0	0.182	0.01
	t_1	8 (8)	0.135	$\frac{1}{2}$	0.318	0.25	0.145	$\frac{1}{2}$	0.317	0.01
Mn	s_2	8 (8)	0.277	0	0.379	0.25	0.275	0	0.387	0.01
	t_2	8 (8)	0.250	$\frac{1}{2}$	0.129	0.25	0.249	$\frac{1}{2}$	0.137	0.01
D	a	1 (1)	0	0	0	6.12	0	0	0	7.80
	d	1 (1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	5.16	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	7.90
D	s_3	4.7(8)	0.217	0	0.095	1.21	0.219	0	0.093	0.25
	t_3	5.3(8)	0.305	$\frac{1}{2}$	0.398	0.02	0.305	$\frac{1}{2}$	0.398	0.02
D	p	4 (8)	0.204	0.464	0	4.55	0.230	0.438	0	2.30
	q	3 (8)	0.291	0.072	$\frac{1}{2}$	1.48	0.304	0.045	$\frac{1}{2}$	1.80
	r_2	6 (8)	0.138	0.138	0.338	3.04	0.141	0.141	0.331	2.83
	r_3	(8)								
	r_4	7 (8)	0.351	0.351	0.131	4.35	0.360	0.360	0.132	2.40
	r_5	(8)								
D	s_4	2.5(8)	0.322	0	0.077	0.40	0.324	0	0.041	1.08
	t_4	(8)								
	u_1	3.5(16)	0.073	0.174	0.166	3.30	0.066	0.177	0.141	2.67
	u_2	8 (16)	0.299	0.385	0.333	0.16	0.296	0.392	0.327	0.20

TABLE IV. Magnetization values in μ_B/Mn atom for Y_6Mn_{23} and $Y_6Mn_{23}D_{23}$. Negative and positive signs indicate directions of the magnetic moments of the Mn atoms.

$Y_6Mn_{23}D_{23}$		$P4/mmm$ structure 78 K	4 K	$N/2$ f.u.	$Fm3m$ structure Y_6Mn_{23}		4 K	$N/2$ f.u.
Mn	b	-3.60	-3.68	1	Mn	b	-3.05	2
	c	$+3.60$	$+3.68$	1				
Mn	e	0	0	2	Mn	d	-2.34	12
	f	0	0	2				
	r_1	0	0	8				
Mn	s_1	0	0	8	Mn	f_1	$+1.99$	16
	t_1	0	0	8				
Mn	s_2	$+2.08$	$+1.60$	8	Mn	f_2	$+1.80$	16
	t_2	-2.08	-1.60	8				
	a_0	9.031	9.030			12.402		
	c_0	12.723	12.722					
	$Z=2$					$Z=4$		
	R_{wp}	9.97	8.64			8.38		
	R_e	6.06	5.81			4.34		
	$\chi=R_{wp}/R_e$	1.64	1.49			1.93		

sition occurring around 175 K in $Y_6Mn_{23}D_{23}$. The crystal structure transforms into a primitive tetragonal structure which can be refined in the space group $P4/mmm$. This structure transformation probably results from the atomic ordering of the deuterium atoms at low temperatures and drives the c axis antiferromagnetic ordering on the Mn sites. $Y_6Mn_{23}D_{23}$ is only weakly antiferromagnetic with the Mn atoms on the b and f_2 sites having finite magnetic moments. In the $P4/mmm$ structure, this corresponds to the Mn moments on the b and t_2 sites coupled antiparallel to those on the c and s_2 sites. No ordered moment was found on the Mn d and f_1 sites in the $Fm3m$ structure.

The comparison between these $Y_6Mn_{23}D_x$ and the $Th_6Mn_{23}D_x$ (Ref. 2) compounds suggests that the Mn-Mn atomic distances do not appear to play a dominant role in determining the overall occurrence of magnetic order in these systems. Instead, deuterium composition and accompanying electronic band effects remain the important factors influencing the magnetic properties.

ACKNOWLEDGMENTS

*Present address: Dow Chemical Company, Midland, MI 48640.

[1]S. K. Malik, T. Takeshita, and W. E. Wallace, Solid State Commun. 23, 599 (1977).

[2]K. Hardman-Rhyne, H. K. Smith, and W. E. Wallace, J. Less-Common Met. (in press).

[3]M. Commandre, D. Fruchart, A. Rouault, D. Sauvage, C. B. Shoemaker, and D. P. Shoemaker, J. Phys. (Paris) Lett. 40, L639 (1979).

[4]C. Crowder, B. Kebe, W. J. James, and W. B. Yellon, in The Rare Earths in Modern Science and Technology, edited by G. J. McCarthy, H. B. Silber, and J. J. Rhyne (Plenum, New York, 1982), Vol. III, p. 473.

[5]A. Delapalme, J. Deportes, R. Lemaire, K. Hardman, and W. J. James, J. Appl. Phys. 50, 1987 (1979).

[6]D. G. Westlake, J. Mater. Sci. 18, 605 (1983); Scr. Metall. 16,

1049 (1982).

[7]I. Jacob, Solid State Commun. 40, 1015 (1981).

[8]H. Kevin Smith (private communication). The deuterium absorption isotherm was obtained at the University of Pittsburgh, Pittsburgh, PA 15260.

[9]R. A. Young, E. Prince, and R. A. Sparks, J. Appl. Crystallogr. 15, 357 (1982).

[10]J. J. Rhyne, Kay Hardman-Rhyne, H. Kevin Smith, and W. E. Wallace, J. Less-Common Met. 94, 95 (1983).

[11]K. H. J. Buschow, Solid State Commun. 21, 1031 (1977).

[12]The magnetic susceptibility is from Ref. 4, and was measured by the extraction method at the Service National des Champs Intense, Grenoble, France.

[13]G. A. Stewart, J. Zukrowski, and G. Wortmann, J. Magn. Magn. Mater. 25, 77 (1981).