Magnetic Structure of TbAg2

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Figure 3 shows a plot of the *para* spin density vs the oxygen spin density for Radicals I–V. A linear relationship is found for the three ketones studied. It is difficult to explain either this linear relationship or the large changes in the relative spin densities of the C–O carbon and the oxygen. A change in the bond angle of the aromatic-substituent bond should produce some change in the π-electron spin densities but the observed change appears to be too large to be explained by this effect.

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Magnetic Structure of $TbAg_2$*

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Neutron-diffraction measurements have revealed that $TbAg_2$ having the tetragonal CaC_2-type structure becomes antiferromagnetic below the Néel temperature of 35°K. The ordered magnetic structure consists of the ferromagnetic sheets which are perpendicular to the *a* axis (face-centered description), and the moment directions of the adjacent ferromagnetic sheets are opposite to one another. All moments are aligned in the direction of the *c* axis, and the saturation moment per Tb is 8.95±0.05 Bohr magnetons which is essentially equal to the ordered moment of the free Tb^{3+} ion. This ordered structure is identical to the commensurable magnetic structure of $TbAu_2$ at temperatures below 42.5°K, but the incommensurable transverse-wavelike spin alignment of $TbAu_2$ found in the 42.5°–55°K range was not detectable in $TbAg_2$. Also, no detectable moment is observed for Ag in $TbAg_2$.

INTRODUCTION

This report is a part of systematic studies on the magnetic and crystal structures of the CaC_2-type crystals by means of neutron diffraction. We have so far reported the results on CaC_2,[1] YC_2,[1] LaC_2,[1] CeC_2,[1,2] PrC_2,[2] NdC_2,[2] TbC_2,[1,2] HoC_2,[2] DyC_2,[3] YbC_2,[1] LuC_2,[1] UC_2,[4] $TbAu_2$,[5] and $AlCr_2$.[6] Except for the dicarbides of Ca, Y, La, Yb, Lu, and U, the magnetically ordered phases have been found in these compounds and their spin structures have subsequently been determined.[2,3,5,6] On previous occasions, we have referred to some unique features of the chemical bonding and of the magnetic properties in these compounds.[1–9] Here, one particular aspect is emphasized as described below.

Let us confine ourselves to the CaC_2-type Tb compounds. In a series, TbC_2,[10] $TbAu_2$,[11] and $TbAg_2$,[11] the *a* lattice constants in the body-centered description are 3.690, 3.707, and 3.710 Å, respectively, whereas the *c* lattice constants are 6.217, 8.987, and 9.226 Å, all at 300°K. One sees readily that the *a* spacings alter slightly, whereas the *c* spacings are considerably different even between $TbAu_2$ and $TbAg_2$. It is one of our purposes to see how the Tb–Tb distance variation due to these progressively different *c* spacings reflects upon the magnetic properties. A brief discussion on this subject is presented. The experimental errors in this paper are expressed in terms of the standard deviation unless otherwise noted.

EXPERIMENTAL AND CRYSTALLOGRAPHIC

The $TbAg_2$ buttons were prepared by arc melting the stoichiometric mixture of terbium and silver, both 99.9% plus pure, and were subsequently homogenized by furnace heating them at 850°C for one day.[11] The buttons were filed and the filings were stress relieved by heating them at 750°C for several hours. Since $TbAg_2$ tarnishes fairly rapidly in air even at room temperature, all the preparatory and handling procedures were carried out in a high vacuum or pure argon or pure helium atmosphere. The chemical analysis of the filings gave 42.1±0.2 and 57.4±0.1 wt % for Tb and Ag, respectively, while the stoichiometric values are 42.4% and 57.6%. The emission spectroscopic analysis did not detect any metallic impurity amounting to more than 0.1%. However, both x-ray and neutron-diffraction patterns exhibit a few faint impurity reflections

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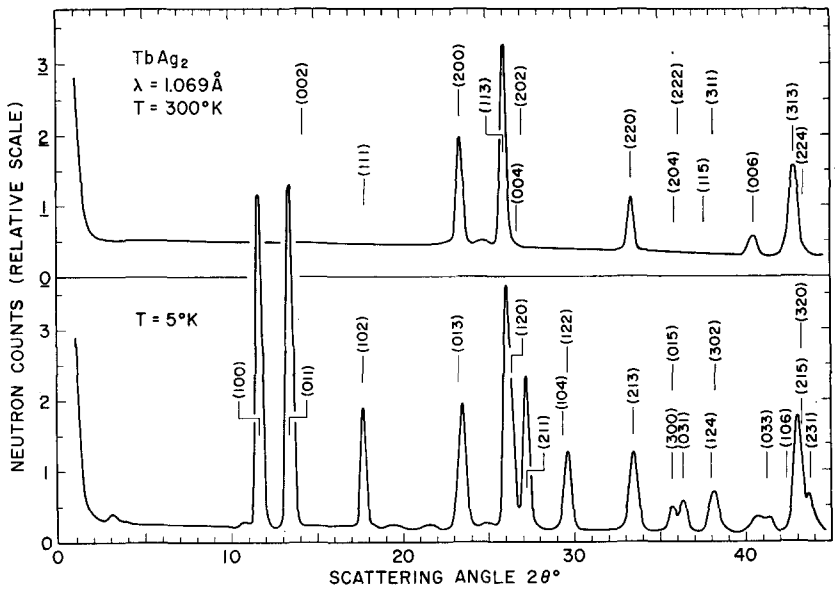

FIG. 1. Neutron-diffraction patterns at 300° and 5°K. The indices for the nuclear reflections are given only in the 300°K pattern and the indices in the 5°K pattern identify the magnetic reflections. These indices are based on the face-centered lattice.

which were not positively identifiable as any probable impurity having a known crystal structure. It was estimated that our neutron samples are at least 98% pure as $TbAg_2$.

The neutron-diffraction data were taken at various temperatures between 300° and 5°K using a multipurpose automatic neutron diffractometer[12] with a setting for the neutron wavelength, $\lambda=1.069$ Å. The low-temperature neutron analysis has confirmed the reported x-ray results[11] that the unit cell dimensions of the tetragonal body-centered lattice are $a'=3.710\pm0.001$ and $c'=9.247\pm0.001$ Å at 300°K, and that there are two TbAg chemical formulas per unit cell in the space group, $D_4j^{17}-I(4/m)mm$. The Ag atoms sites are $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2})\pm(00z)$, whereas the Tb atoms take the special positions, $z=0$. No evidence for a crystallographic transformation was observed in the 300°–5°K range. Our unit cell dimensions at 5°K are $a'=3.698\pm0.003$ and $c'=9.226\pm0.005$ Å. The linear thermal-expansion coefficients in the 5°–300°K range are then obtained as 11 ± 3 and 8 ± 2 in 10^{-6} deg^{-1} along the a' and c' axes, respectively. As in the case of $TbAu_2$,[5] the ordered magnetic structure of $TbAg_2$ is described in terms of the face-centered lattice and hence hereafter we refer to the unit cell having the dimensions, $a=\sqrt{2}a'$ and $c=c'$.

As regards the nuclear reflections, in addition to the face-centered extinction rule, the reflections for which $l\neq3n$ are hardly detectable in the range $0<(\sin\theta)/\lambda<0.6$ Å^{-1} (Fig. 1). The coherent scattering amplitudes of Tb and Ag are 0.76 [13] and 0.61 [14] in 10^{-12} cm, respectively. Hence, the structure factor per $TbAg_2$ is expressed as $F=0.76+1.22\cos2\pi lz$. Consequently, the positional parameter z should be in the vicinity of $\frac{1}{3}$ so as to explain the observed intensities. Because of this special positional parameter and because of peak overlapping, two equally probable z parameters, 0.341 or 0.326,[15] were obtained with a large uncertainty of ±0.003. The resultant temperature factor coefficients, $2B$ in $\exp[-2B(\sin\theta/\lambda)^2]$, are 1.3 ± 0.2 and 0.3 ± 0.1 Å^2 at 300° and 5°K, respectively. In Table I, the observed nuclear intensities are compared with the calculated values for two probable z parameters leading to essentially the same agreement factor,

$$R=\sum|I_{\rm obs}-I_{\rm calc}|/\sum I_{\rm obs},$$

of about 4%.

MAGNETIC STRUCTURE

Paramagnetic scattering of $TbAg_2$ at 300°K exhibits a small short-range order modulation. Upon cooling, the short-range modulation is steadily enhanced and appears to cease at 35°K. Temperature dependence of the short-range order modulation resembles, to a certain extent, the TbC_2[2] and $TbAu_2$[5] cases. At $34.8°\pm0.5°$K, a set of coherent peaks starts to grow. These magnetic peaks could be indexed on the basis of the face-centered chemical lattice. The observed magnetic indices satisfy the criteria, $h+l$ odd and $k+l$ odd (Fig. 1). Hence, the moments of the Tb atoms on the planes perpendicular to the a axis should be aligned ferromagnetically, and

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[15] The close-neighbor interatomic distances in angstroms at 300°K are Tb–8Tb (along the [101]-type axes) $=5.316\pm0.001$, Tb–2Ag (along the c axis) $=3.15(3.01)\pm0.03$, Tb–8Ag $=3.007(3.078)\pm0.002$, Ag–Ag′ (along the c axis) $=2.94(3.22)\pm0.06$, Ag–4Ag″ $=3.12(2.98)\pm0.03$, where two alternative values correspond to $z=0.341$ and 0.326, and those based on the latter parameter are given in parentheses.

TABLE I. Observed and calculated intensities (barns/mole) of the nuclear reflections of $TbAg_2$ at 300°K.[a]

Indices	I_{calc} ($z=0.341$)	I_{calc} ($z=0.326$)	ΣI_{calc}	I_{obs}
002	4	(0)		<7
111	2	(7)		<7
200	184	(184)		173
113	296	(295)		305
004	0	(2)	4(2)	<7
202	4	(0)		
220	90	(90)		89
204	0	(5)	2(5)	<7
222	2	(0)		
115	5	(0)	6(3)	~8
311	1	(3)		
006	29	(29)		32
313	214	(214)	214(217)	212
224	0	(3)		
206	85	(84)	128(127)	136
400	43	(43)		
402	1	(0)	7(6)	~8
117	0	(5)		
315	6	(0)		
331	0	(1)		
226	66	(66)	133(133)	128
420	67	(67)		
008	1	(0)	64(65)	63
333	63	(63)		
404	0	(2)		

[a] The calculated values in parentheses are those for $z=0.326$. The indices are based on the face-centered description.

the moment directions of the adjacent ferromagnetic sheets are opposite to one another. The intensity computation affirmed that the moment direction is parallel or antiparallel to the c axis. The resultant magnetic structure is illustrated in Fig. 2.

Temperature dependencies of three representative magnetic reflections, (100), (011), and (102), differ insignificantly from one another and their averaged-out data are shown in Fig. 3. The observed temperature-intensity curve deviates slightly from the Brillioun curve for $S=\frac{1}{2}$ as seen in Fig. 3. However, the difference here is of doubtful significance. Observed and calculated magnetic intensities at 5°K are listed in Table II, where the magnetic form factor is obtained from the Hartree–Fock values[16] and the R factor is 3%.

It is probable that the Ag atoms in $TbAg_2$ may have small, localized long-range ordered moments at low temperatures. No evidence of such moment was observed. The detectable upper limit here is about 0.3 Bohr magnetons per Ag, assuming that the Ag moment alignment is similar to the Tb moment structure described above.

As reported recently,[5] $TbAu_2$ exhibits a linear-transverse-wave spin alignment in the range 55°–42.5°K (α phase). This static moment wave (or spin density wave) is propagated along the a axis and is polarized in the c-axis direction. The wavelength of this moment wave is incommensurable with the atomic repetition. At 42.5°K, however, a clear-cut first-order magnetic transition takes place and the wavelength of the moment wave becomes abruptly equal to the a spacing. This commensurate magnetic structure of $TbAu_2$ (β phase) is identical to the ordered magnetic structure of $TbAg_2$. Consequently, it is rather a natural speculation that, in an analogy to the $TbAu_2$ case, $TbAg_2$ may also have an incommensurate α magnetic phase with a very small moment. A careful search for the incommensurate phase was then carried out. Nearly a dozen diffraction patterns near the Néel temperature were examined so as to decrease the statistical error. The effort was in vain, and nothing but a single ordered phase was detectable. It is estimated that, if the noncommensurate phase exists, its root-mean-square ordered moment should be less than 0.15 in Bohr magneton.

The Néel temperatures of TbC_2,[2] $TbAu_2$,[5] and $TbAg_2$ are 66°, 55°, and 35°K, respectively. This implies a decreasing exchange interaction in this order, in accordance with the increasing Tb–Tb separations due to the increasing c spacing as stated in the Introduction. The type I ordered magnetic structure of TbC_2 may be described in terms of linear, transverse moment waves propagating along the body-centered a' axis and polarized strongly in the c-axis direction. The wavelengths

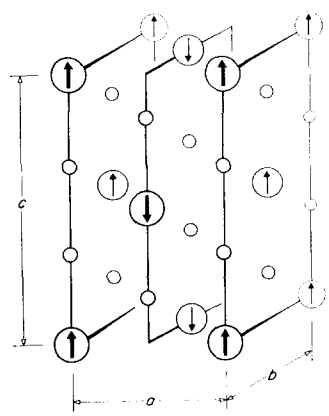

FIG. 2. A schematic representation of the ordered magnetic structure of $TbAg_2$. Larger circles with the moment arrow represent the Tb atoms and smaller circles assume the Ag atoms.

[16] M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. **37**, 1245 (1962); **41**, 1878 (1964).

of the TbC_2 moment waves are approximately equal to $4\times(a'$ chemical spacing), and in a generalized sense it may be classified as an incommensurate type.[17] At temperatures below about 35°K, TbC_2 exhibits a complex magnetic ordering (type II) which is also of noncommensurate type.[17] The noncommensurate phase in $TbAu_2$ is stable in a much narrower temperature range than the TbC_2 case and no such phase was observed in $TbAg_2$. It appears that the longer Tb–Tb distances due to the longer c spacing tend to wipe out the incommensurate phase. In any event, the static moment waves in all cases of our concern are of linear, transverse mode propagating in the direction perpendicular to the c axis and are strongly or completely polarized in the c-axis direction. Temperature dependencies of the magnetic intensities of the type I structure of TbC_2, those of the β structure of $TbAu_2$ and the $TbAg_2$ case are all closely approximated by the Brillouin function with $S=\frac{1}{2}$.

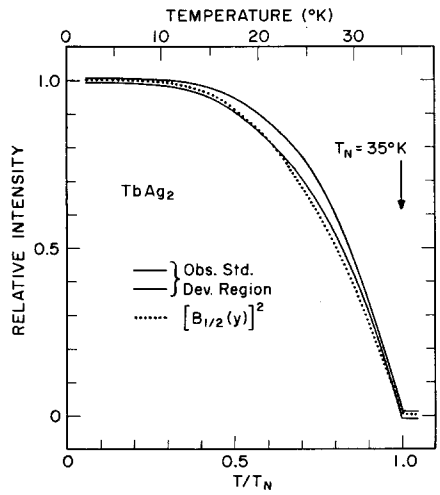

FIG. 3. Temperature-intensity relation of the magnetic reflection of $TbAg_2$. A number of data obtained from three magnetic reflections are averaged out here and the solid contour lines approximate the standard deviation boundaries. The square of the Brillouin function for $S=\frac{1}{2}$ is also shown for comparison.

[17] In Ref. 2, it was stated that the wavelength of the static moment wave found in the type I phase of TbC_2 is *equal* to $4\times(a'$ spacing). It should have stated that the type I wavelength of TbC_2 is *closely approximated* by $4a'$, since the accuracy attainable from the satellite reflections in the powder pattern is hardly capable of concluding an exact equality. The type II structure of TbC_2 has recently been proved to be a noncommensurate one also [M. Atoji (unpublished)].

TABLE II. Observed and calculated magnetic intensities (barns/mole) of $TbAg_2$ at 5°K.[a]

Indices	I_{calc}	ΣI_{calc}	I_{obs}
100	511		515
011	569		568
102	176		180
013	53		51
120	148		150
211	256		243
104	18	188	175
122	170		
213	97		92
300	31		
015	7	94	98
031	56		
124	50	93	95
302	43		
033	29		36
106	3		
320	33	122	138
215	25		
231	61		
304	18	68	66
322	50		

[a] The indices are based on the face-centered lattice.

As it has been repeatedly pointed out,[2,5] the magnetic properties of $MnAu_2$[18] are completely dissimilar to those described above, despite the fact that in the crystal-structure category there is hardly any substantial difference among $MnAu_2$ and our compounds. Here, for a comparative purpose, the helical magnetic spin alignment of $MnAu_2$ is interpreted in terms of two linear transverse moment waves, both of which are propagating along the c axis. These two waves are represented by $(gJ)\cos(102°\ z/c)$ and $(gJ)\sin(102°\ z/c)$, the former being polarized in the a-axis direction and the latter in the b-axis direction.

ACKNOWLEDGMENTS

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