

## Magnetic Order in Rare-Earth Intermetallic Compounds

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Neutron diffraction measurements were made on a series of rare-earth intermetallic compounds to determine the type of magnetic order and its relationship to the number of valence electrons in the system. The compounds studied included TbCu, TbZn, TbGa, TbAg, TbHg, and TbIn. The compounds with Cu, Zn, Ag, and Hg were found to have the CsCl-type structure, TbGa the CrB-type structure, and TbIn a complex tetragonal unit cell. TbGa is ferromagnetic with a Curie temperature of 155°K, while TbIn is antiferromagnetic below 190°K. For the compounds with the CsCl structures, TbCu and TbAg are antiferromagnetic with Néel temperatures of 115 and 100°K, while TbZn and the TbHg are ferromagnetic below 160 and 80°K, respectively. This difference in magnetic behavior of the compounds with group Ib and IIb metals must be associated with the number of valence electrons rather than with interatomic separations because the lattice constants of the two groups overlap.

### INTRODUCTION

MUCH of the recent interest in the rare-earth metals and alloys is related to the interaction mechanism responsible for the magnetic coupling between the rare-earth atoms. Because of the small radial extent of the  $4f$  wave functions, it is generally assumed that direct exchange cannot be important for these materials and that an indirect exchange via the conduction electrons is responsible for the observed magnetic phenomena. In that event, one might expect the coupling to be sensitive to the number of conduction electrons for rare-earth compounds. One of the simplest crystal systems in which the number of conduction electrons can be varied is that of the CsCl type. Many of the RX compounds formed between the rare earths and elements from groups Ib, IIb, and IIIb have this structure. This neutron diffraction study was undertaken to determine the type of magnetic order and its relationship to the number of valence electrons for some of these compounds.

### EXPERIMENTAL

The following compounds were prepared: TbCu, TbZn, TbGa, TbAg, TbHg, and TbIn. Terbium was selected as the rare-earth constituent because of its low-absorption cross section for thermal neutrons and its high-spin value and consequent strongly interacting magnetic ions. All samples, with the exception of TbZn and TbHg were prepared by arc melting of stoichiometric amounts of the constituents. Weight losses during melting were negligible so that nominal concentrations were accepted. X-ray examinations showed the CsCl-type structure for TbCu and TbAg, the CrB-type structure for TbGa and a complex tetragonal unit cell for TbIn. The CsCl structure has been reported<sup>1</sup> for GdIn and DyIn, but it was not indicated whether these were "as-cast" or annealed samples. The TbIn filings were annealed at 900°C for 3 h and re-examined. There was no detectable differ-

ence in the x-ray patterns of the unannealed and annealed samples. The TbZn and TbHg compounds were prepared by solid-state-vapor-state reaction using 80-mesh Tb filings along with the proper amounts of Zn and Hg in evacuated quartz capsules. The TbZn was initially heated at 700°C for 4 h, then ground to a powder and reheated. This procedure was repeated until a reaction product of suitable quality was obtained. A similar procedure was followed for TbHg except that the initial heat treatment was at 400°C for 24 h. A single-phase material was not obtained in this case, but the reaction was carried out until about 80% of the sample was of the desired CsCl-type

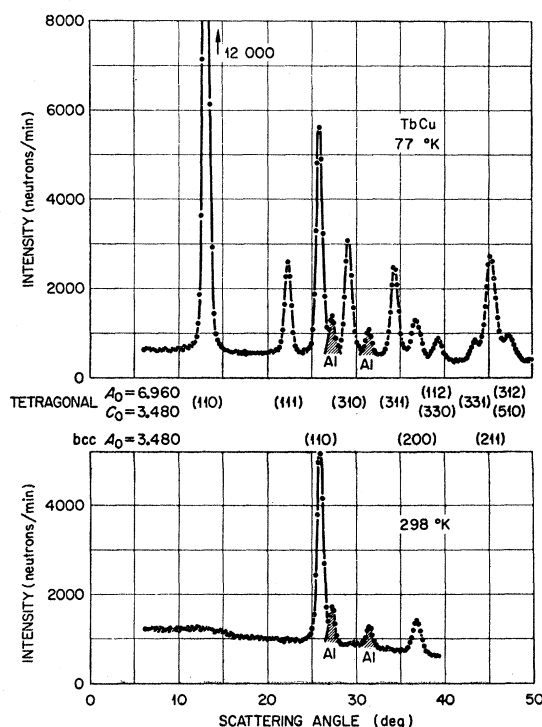


FIG. 1. Neutron powder diffraction patterns of TbCu at 298 and 77°K.

<sup>1</sup>N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.* 14, 948 (1961).

structure. Chemical analyses showed 48.2 and 48.5 at.% Tb for the TbZn and TbHg samples.

Neutron diffraction data were obtained at sample temperatures from 4.2–298°K for all of these samples. Typical results for the antiferromagnetic compounds are shown in Fig. 1 in which the lower curve is a pattern obtained for TbCu at 298°K. Even though the alloy is positionally ordered, the superlattice lines do not appear because the nuclear scattering amplitudes of Tb and Cu are so nearly the same. An additional set of reflections are apparent in the upper pattern, taken at 77°K, and these have been indexed on the basis of a magnetic unit cell doubled along two cube edges. This is suggestive of an antiferromagnetic structure of the  $(\pi, \pi, 0)$  type<sup>2</sup> in which adjacent ferromagnetic (110) planes of moments are oppositely oriented.

Absolute magnetic intensities were obtained by an internal calibration with the nuclear intensities using the nuclear scattering amplitudes tabulated by Wilkin-

TABLE I. Summary of results for TbCu and TbAg.

<i>hkl</i>	TbCu			TbAg		
	$\sin\theta/\lambda$	$\mu f^a$	$\mu^b$	$\sin\theta/\lambda$	$\mu f^a$	$\mu^b$
(110)	0.102	8.5	8.9	0.098	8.7	9.1
(111)	0.176	7.8	9.0	0.169	7.9	9.0
(310)	0.227	7.0	8.9	0.218	7.0	8.7
(311)	0.269	6.4	8.8	0.258	6.4	8.6
(112), (330)	0.305	5.5	8.2	0.293	5.5	8.0
(331)	0.337	5.2	8.5	0.324	5.2	8.2
(312), (510)	0.366	4.5	7.9	0.352	4.5	7.6
(511)				0.378	4.2	7.6
$a_0$ (Å)	3.480			3.622		
$T_N$ (°K)	115			100		

<sup>a</sup> Internally calibrated from the nuclear intensities. Assumes the  $(\pi, \pi, 0)$  structure and moment alignment parallel to the *c* axis. The following nuclear scattering amplitudes were used;  $b_{Tb} = 0.75$ ,  $b_{Cu} = 0.79$  and  $b_{Ag} = 0.61 \times 10^{-12}$  cm.

<sup>b</sup> From  $\mu f$  values assuming the Tb<sup>3+</sup> form factor calculated by Blume, Freeman, and Watson (Ref. 4).

son, Wollan, and Koehler.<sup>3</sup> This calibration was made at low temperatures and included absorption and thermal-motion corrections. The resultant magnetic intensities were converted to  $\mu f$  values (where  $\mu$  is the ordered moment and  $f$  the magnetic form factor) on the assumption of the  $(\pi, \pi, 0)$  magnetic moment configuration with moment alignment parallel to the *c* axis of the magnetic unit cell. The results are given in Table I along with moment values obtained by the assumption of the Tb<sup>3+</sup> form factor calculated by Blume, Freeman, and Watson.<sup>4</sup> The agreement is such as to support the assumption of the  $(\pi, \pi, 0)$  antiferromagnetic structure. The smaller moment values obtained at the higher  $\sin\theta/\lambda$  values indicate that the Tb<sup>3+</sup> form factor in TbCu falls off more rapidly than

<sup>2</sup> H. A. Gersch and W. C. Koehler, Phys. Chem. Solids 5, 180 (1958).

<sup>3</sup> M. K. Wilkinson, E. O. Wollan, and W. C. Koehler, Ann. Rev. Nucl. Sci. 11, 303 (1961).

<sup>4</sup> M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. 37, 1245 (1962).

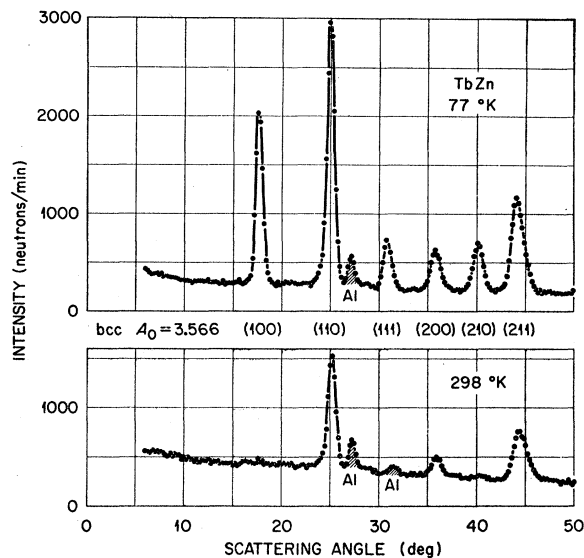


FIG. 2. Neutron powder diffraction patterns of TbZn at 298 and 77°K.

that calculated for the free ion. Similar effects have been previously observed in other rare-earth samples.

Similar results were obtained for TbAg and these are included in Table I. Here also the  $(\pi, \pi, 0)$  structure with moment alignment parallel to the *c* axis was required to account for the magnetic intensities.

The neutron diffraction result for the Zn and Hg compounds are illustrated by the TbZn patterns in Fig. 2. The lower curve shows the 298°K data in which only the body-centered cubic lines are observed. Here again the superlattice lines are absent because the nuclear scattering amplitudes of Tb and Zn are nearly the same. At 77°K, additional reflections were observed and these are shown in the upper curve. These reflections can be indexed on a cubic cell of the same size as the chemical cell indicating ferromagnetic order for this compound.

Absolute magnetic intensities were obtained by internal calibration with the nuclear intensities using the nuclear scattering amplitudes of Ref. 3. Since the nuclear and magnetic intensities were superimposed, thermal corrections to the 298° nuclear data were necessary in order to obtain the magnetic intensities at 4.2°K. These corrections were made with a Debye characteristic temperature of 140°K. Moment values were obtained on the assumption of 1:1 stoichiometry, ferromagnetic order and the calculated Tb<sup>3+</sup> form factor.<sup>4</sup> These are given in Table II along with similarly obtained results for TbHg. In comparing the results, it should be noted that the moment values from the superlattice reflections (100), (111), and (210) are the more reliable since negligible thermal corrections were required for these. The results are in reasonable agreement, although the moment values are lower than the expected  $9 \mu_B$ .

TABLE II. Summary of results for TbZn and TbHg.

<i>hkl</i>	TbZn			TbHg		
	$\sin\theta/\lambda$	$\mu^a$	$\mu^b$	$\sin\theta/\lambda$	$\mu^a$	$\mu^b$
(100)	0.140	7.1	7.8	0.136	7.1	7.7
(110)	0.198	6.7	8.0	0.193	7.5	8.9
(111)	0.243	5.7	7.4	0.236	5.8	7.5
(200)	0.281	5.7	8.1	0.273	7.3	10.2
(210)	0.314	5.3	8.1	0.305	4.9	7.4
(211)	0.344	4.1	6.8	0.334	5.3	8.6
$a_0$ (Å)	3.566			3.678		
$T_c$ (°K)	160			80		

<sup>a</sup> Internally calibrated from the nuclear intensities using the following scattering amplitudes;  $b_{Tb} = 0.75$ ,  $b_{Zn} = 0.61$ , and  $b_{Hg} = 1.3 \times 10^{-12}$  cm. Thermal corrections were made using Debye temperatures of 140°K for TbZn and 160°K for TbHg.

<sup>b</sup> From  $\mu^a$  values assuming the Tb<sup>3+</sup> form factor calculated by Blume, Freeman, and Watson (Ref. 4).

Results for TbGa are summarized in Table III. The crystal structure is of the orthorhombic CrB type<sup>5</sup> with  $a_0 = 4.33$ ,  $b_0 = 10.90$ , and  $c_0 = 4.09$ . The space group is  $Cmcm$  with both atoms at  $4(c) \pm (0, y, \frac{1}{4}) + (000, \frac{1}{2}, 0)$  with  $y(Tb) = 0.141$  and  $y(Ga) = 0.426$ . The compound is ferromagnetic with a Curie temperature of 155°K. The integrated intensities, expressed in arbitrary units, are given in Table III. Calculated intensities were normalized to the more intense nuclear reflections. The magnetic intensities were calculated assuming  $9 \mu_B$  per

TABLE III. Comparison of observed and calculated intensities from TbGa.

<i>hkl</i>	Nuclear		Magnetic	
	$P_{hkl}^a$ (calc)	$P_{hkl}$ (obs)	$P_{hkl}^b$ (calc)	77°K $P_{hkl}$ (obs)
020	41	27	66	77
110	16	23	672	805
021	10	10	363	347
111	753	801	1319	1381
130				
040				
131	604	530	170	209
041				
200	180	229	176	246
002	175	171	11	37
220				
150	22	23	22	25
022				
060				
112	26	23	671	661
221				
151				
240	365	334	362	360
061				
312				
042	176	154	33	53
241				
202				
170	351	278	153	156

<sup>a</sup> For CrB-type structure with  $y(Tb) = 0.141$  and  $y(Ga) = 0.426$  and  $b_{Tb} = 0.75 \times 10^{-12}$  cm,  $b_{Ga} = 0.72 \times 10^{-12}$  cm (normalized to the more intense nuclear reflections).

<sup>b</sup> For a ferromagnet with magnetic moments of  $9 \mu_B/Tb^{3+}$  aligned parallel to the  $c$  axis. The calculated Tb<sup>3+</sup> form factor (Ref. 4) was used along with an experimentally determined relative magnetization at 77°K of 0.768. (Normalized to the more intense nuclear reflections.)

<sup>5</sup> N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.* **14**, 946 (1961).

Tb<sup>3+</sup> ion aligned parallel to the  $c$  axis. The calculated Tb<sup>3+</sup> form factor<sup>4</sup> was used along with an experimentally determined relative magnetization at 77°K of 0.768. The agreement is reasonably good for both the nuclear and magnetic intensities. The TbIn alloy was found to be antiferromagnetic below 190°K but since the crystal structure has not been determined those results have been omitted.

## DISCUSSION

This experiment shows that TbCu and TbAg assume a type of magnetic order different from that of TbZn and TbHg. The first two compounds were found to be antiferromagnetic with the  $(\pi, \pi, 0)$  type of structure and the last two ferromagnetic. This difference in the magnetic behavior of the two groups cannot be attributed to internuclear separations because the lattice constants of the two groups overlap. The two types of magnetic behavior are then to be associated with the number of valence electrons; antiferromagnetic when the rare earth is combined with a group Ib metal, ferromagnetic when combined with a group IIb metal. In a recent paper, Mattis and Donath<sup>6</sup> calculated the magnetic ground states for a simple cubic structure assuming a Ruderman-Kittel-Yosida type of interaction. They found transitions from ferromagnetism through a series of increasingly antiferromagnetic structures as the number of conduction electrons increased. These antiferromagnetic structures were the  $(\pi, 0, 0)$ ,  $(\pi, \pi, 0)$ , and  $(\pi, \pi, \pi)$  types in the designation of Gersch and Koehler.<sup>2</sup> In these CsCl-type structures the rare-earth ions occupy the sites of a simple cubic lattice, so that these calculations might be regarded as applicable to these systems. It is interesting to note that two of the calculated ground states were observed in this series of compounds. However, the calculations were made only for values of the Fermi wave vector ( $k_F$ ) out to the edge of the first Brillouin zone, and in this region the sequence of magnetic ground states with increasing  $k_F$  values is the reverse of that observed. A more direct comparison must await the extension of the calculations to the larger  $k_F$  values appropriate to these systems,<sup>7</sup> but the array of antiferromagnetic structures predicted by the calculations of Mattis and Donath suggest that these observations may be accounted for on the basis of a Ruderman-Kittel-Yosida type of indirect exchange interaction.

## ACKNOWLEDGMENTS

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<sup>6</sup> D. Mattis and W. E. Donath, *Phys. Rev.* **128**, 1618 (1962).

<sup>7</sup> Note added in proof. It was recently brought to the attention of the authors that this extension of the calculations has been made (D. Mattis, N. Anthony, and L. Horwitz, IBM Research Report RC-945, May 23, 1963). These calculations indicate a stable ferromagnetic state for the  $k_F$  values appropriate to these compounds. This agrees with the observations for TbZn and TbHg but not for TbCu and TbAg.