STRUCTURE AND MAGNETIC PROPERTIES OF TbB_4

C. M. McCarthy and C. W. Tompson
Department of Physics and Research Reactor

F. K. Ross
Research Reactor and Department of Chemistry
University of Missouri, Columbia, Mo. 65211

Z. Fisk
Institute for Pure and Applied Physical Sciences
University of California-San Diego, La Jolla, Ca. 92093

ABSTRACT

Neutron powder diffraction analysis and single-crystal studies of TbB_4 indicate that this compound is isostructural with ErB_4 and DyB_4 but has a different magnetic structure. The magnetic moments of the Tb atoms appear to lie in mixed antiferromagnetic domains of approximately [301] and [031] orientation.

INTRODUCTION

In a systematic study of rare-earth borides,[1] poly-crystalline samples of TbB_4 (97% ^{11}B enriched) were studied by powder neutron diffraction and Rietveld refinement techniques. The compound is isostructural with ErB_4 and DyB_4 at all temperatures investigated (78K, 28K and 4.2K) but the magnetic structure differs from the c-axis antiferromagnetic ordering reported[2] for the latter compounds. The powder diffraction data (Fig. 1) suggest a magnetic model containing antiferromagnetic ordering in (hk0) with mixed domains required to preserve tetragonal symmetry (Fig. 2). This assignment is based on

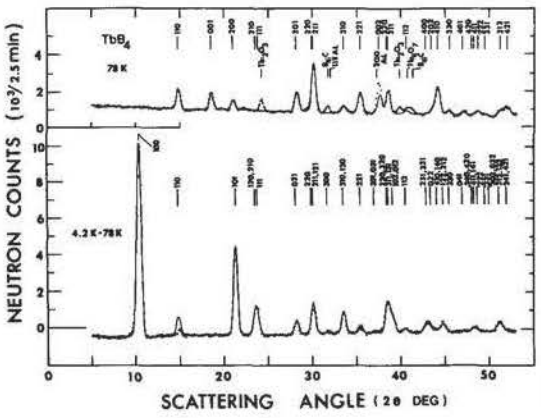

Fig. 1. TbB_4 powder diffraction data.

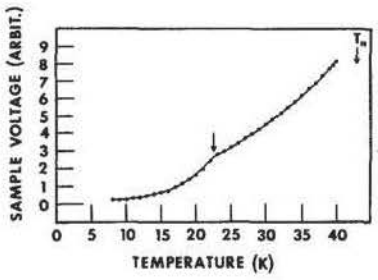

Fig. 2. Single-crystal electrical resistivity data for TbB_4.

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the large intensity of the 100 reflection compared to the 011; the 00ℓ reflections with ℓ odd are extinguished by virtue of the z = 0 coordinate for all Tb atoms. Rietveld refinement of the 4.2K data with this structure gave poorer results than obtained for the other rare-earth borides in the study. This was partly attributed to obvious sample contamination by terbium oxides and by B_4C (Fig. 1), but the Rietveld residual for the magnetic structure (10%) was dominated by the fit of peaks free from overlap with the contaminants. In addition, electrical resistivity measurements made on TbB_4 single-crystals show a discontinuity at 23K (Fig. 2), but comparison of the 28K and 4.2K diffraction data did not reveal any differences in the crystal or magnetic structures. After obtaining single crystals of TbB_4, we initiated further studies using 3-dimensional diffraction data to define the magnetic structure of this material better.

EXPERIMENTAL

A well-formed polyhedron of TbB_4 (97% ^{11}B) showing 28 developed faces was used and was approximated as a sphere of 1.05 mm diameter for absorption and extinction corrections. Data were collected at 298K and 8K; after standing at 298K for several weeks, further data were collected at 78K and 28K. Averaging of the symmetry-equivalent reflections shows good internal agreement for all data except the 28K data (Table I). The latter data contain more internal variation but do not conclusively depart from 4/m mm symmetry. All data were collected on the 2XE instrument (at MURR) which is equipped with a 40 cm i.d. Huber circle and a Displex cryostat.

TABLE I. Single-crystal data for TbB4

Temperature	Form	No. of Data	Stability	Data Averaging R(F)	$R_w(F)$	No. of Data for least-squares
298K	hkℓ	367	±0.9%	0.023	0.021	183
78K	±hkℓ	710	±1.8%	0.021	0.019	194
28K	±hkℓ	713	±1.6%	0.034	0.042	197
8K	hkℓ	362	±0.6%	0.019	0.017	191

ANALYSIS

The data were modeled using standard crystallographic least-squares methods with locally-introduced modifications. The 78K data were used to obtain reference parameters for atom positions, anisotropic thermal motion and anisotropic extinction. These parameters were then used as constraints for the data at other temperatures; only an overall scale factor and one isotropic thermal parameter, adjusted to compensate for changes in thermal motion, were used in the fitting of this model. For magnetic structures, the least-squares symmetry operations were replaced by 95 parameter constraints. This permitted the generation of a magnetic cell having the same size as but different symmetry form the crystal cell. Magnetic atoms were entered as two contributions with different symmetry constraints but with identical positional and thermal parameters. The projection of magnetic domains onto the scattering planes was programmed as a fixed

calculation which was modified for reassignment of the magnetic vectors. Results of these models are tabulated in Table II.

TABLE II. Results of least-squares model refinement

Temperature	80K	298K	298K	28K	28K	8K	8K	8K
Model	(1)	(2)	(1)	(2)	(3)	(2)	(3)	(4)
R(F)	.0296	.0341	.0318	.123	.060	.199	.099	.090
Rw(F)	.0290	.0365	.0392	.255	.088	.262	.167	.125

(1) Standard crystallographic model. Variables are scale, atom coordinates and anisotropic temperature factors and anisotropic extinction.
(2) Constrained model. 80K parameters, scale and overall temperature factor.
(3) Constrained model (2) + magnetic atoms with variable occupancy and (100-010) projection.
(4) Constrained model (3) with (301-031) projection.

The extrapolation of the 78K parameters to 298K with a scale and a single parameter for thermal compensation gave good results. This model was applied to the 28K and the 8K data and magnetic scattering was introduced to minimize the residuals. Although this model can be altered to allow for a reduction in the symmetry of the crystallographic cell (by redefining some of the 95 constraints mentioned above), no evidence was found to justify a modification in the crystal structure. The nuclear cell is centrosymmetric and the magnetic cell has only B component contributions to the structure factors; this provides convenient identification of model effects and the fit of special reflections (h0ℓ with h even is purely nuclear while h odd receives only magnetic contributions). Comparisons of magnetic contributions referenced to various scattering directions gave best results for domains in the (h0ℓ) plane (and thus an equal mixture of (0kℓ) domains) with a minimum residual occurring approximately along [301].

CONCLUSIONS

The residual discrepancies in the fit of the 8K data appear to be predominantly in the magnetic model. The absence of any superlattice reflections constrains all magnetic models to coincide with the nuclear cell. Although the best fit occurs with an added ℓ-axis tilt of 20-30°, the R-factor obtained (9%) is higher than expected for the internal consistency of the 8K data. Modified Fourier mapping techniques are being employed to investigate this model further. In addition, the inconsistencies observed at 28K are probably due to unequal domain formation or annealing. These will be studied in future experiments.

REFERENCES

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