A neutron diffraction demonstration of long-range magnetic order in the quasicrystal approximant DyCd6

D. H. Ryan
McGill University

J. M. Cadogan
Australian Defence Force Academy

Tai Kong
Iowa State University and Ames Laboratory

Follow this and additional works at: https://lib.dr.iastate.edu/ameslab_manuscripts

Part of the Engineering Physics Commons, and the Materials Science and Engineering Commons

Recommended Citation
Ryan, D. H.; Cadogan, J. M.; and Kong, Tai, "A neutron diffraction demonstration of long-range magnetic order in the quasicrystal approximant DyCd6" (2019). Ames Laboratory Accepted Manuscripts. 572. https://lib.dr.iastate.edu/ameslab_manuscripts/572

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
A neutron diffraction demonstration of long-range magnetic order in the
quasicrystal approximant DyCd6

Abstract
We have used neutron powder diffraction to demonstrate the existence of long-range antiferromagnetic
order of Ising-like Dy moments in the DyCd6 quasicrystal approximant phase. This cubic compound
undergoes a slight distortion to a monoclinic cell at low temperatures. The Neel temperature is 18.0(2) K
and the magnetic order of the Dy sublattice may be described in the parent cubic Im (3) over bar structure
using a combination of two propagation vectors, k(1) = [0 0 0] and k(2) = [1/2 0 1/2], yielding 'anti-I' order.
Alternatively, when referred to the monoclinic C2/c cell, the magnetic structure may be described by a
single propagation vector: k = [1 0 0].

Disciplines
Engineering Physics | Materials Science and Engineering

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/ameslab_manuscripts/572
A neutron diffraction demonstration of long-range magnetic order in the quasicrystal approximant DyCd$_6$

D. H. Ryan, J. M. Cadogan, T. Kong, P. C. Canfield, A. I. Goldman, and A. Kreyssig

COLLECTIONS

Paper published as part of the special topic on 2019 Joint MMM-Intermag Conference and Collection
A neutron diffraction demonstration of long-range magnetic order in the quasicrystal approximant DyCd\textsubscript{6}

I. INTRODUCTION

The cadmium-rich side of most rare-earth (R) cadmium alloy phase diagrams contains RCd\textsubscript{6}, a 1/1 cubic approximant based on a bcc packing of interpenetrating Tsai-type icosahedral clusters. These clusters are the building blocks of two remarkable families of thermodynamically stable binary quasicrystalline rare-earth containing phases: YbCd\textsubscript{5.7} and RCo\textsubscript{6.5} (R = Gd – Tm, Y) that lie either side of the cubic RCo\textsubscript{6} phase. Together, these three systems provide an invaluable window onto the properties of quasicrystalline materials. As stable binary compounds they greatly simplify preparation and structural analysis. The presence of large, local-moment rare-earths opens the possibility of studying magnetic ordering in a quasiperiodic environment – is long-ranged magnetic order compatible with such structures? The existence of periodic approximant phases that are close both in structure and composition means that almost-direct comparisons can be made between the behaviour of a periodic and a quasiperiodic compound.

Perhaps surprisingly, the properties of the RCo\textsubscript{6} compounds are quite complex, with most undergoing a structural change from cubic to monoclinic near 170 K\textsuperscript{5} and many exhibiting multiple features in heat capacity (C\textsubscript{p}) and susceptibility (\chi) at much lower temperatures that likely reflect magnetic ordering.\textsuperscript{5} Indeed, the sharp nature of the features in C\textsubscript{p} and \chi\textsuperscript{1,5,6} have been interpreted as evidence for long-ranged magnetic order rather than the spin-glass-like behaviour observed in most other quasicrystalline systems.\textsuperscript{5} The rather large neutron absorption cross-section of natural cadmium has discouraged direct searches for long-ranged magnetic order in the RCo\textsubscript{6} system by neutron diffraction, however x-ray resonant magnetic scattering (XRMS) has been used to demonstrate that both TbCd\textsubscript{6} and HoCo\textsubscript{6} adopt long-ranged antiferromagnetic structures below their respective Néel temperatures of 24 K and 8.5 K.\textsuperscript{5}

Here we present a neutron powder diffraction study of a DyCd\textsubscript{6} sample prepared using natural cadmium and employing a large-area flat-plate technique\textsuperscript{9} to reduce the impact of absorption by...
cadmium. We find that below $T_N=18$ K, DyCd$_6$ is antiferromagnetically ordered in a structure that breaks the body centering symmetry of the underlying bcc crystal structure such that dysprosium moments associated with the cube-corner clusters are coupled antiparallel to those associated with the cube-centre clusters. The magnetic diffraction peaks show no additional broadening relative to the nuclear Bragg peaks, indicating that the magnetic correlations are at least long-ranged. These results are fully consistent with the earlier XRMS data on TbCd$_6$ and HoCd$_6$.

II. EXPERIMENTAL METHODS

The DyCd$_6$ sample was prepared at Ames Laboratory using the method outlined by Das et al. CuK$_\alpha$ x-ray diffraction confirmed the single-phase nature of the sample with the body-centred cubic Im3 ($\#204$) space group. Magnetic characterization was carried out on a Quantum Design Magnetic Properties Measurement System (MPMS) equipped with a 9 T magnet and operated down to 1.8 K.

The crystal structure of RCd$_6$ is cubic Im3 ($\#204$) at ambient temperatures. Dy occupies the 24g site while Cd occupies several sites (12d, 12e, 16f, 24g). It is known that this structure undergoes a slight distortion to a low temperatures monoclinic $\text{Ca}_2/c$ ($\#15$) cell with unit cell sides of $\sqrt[3]{a}$ and a monoclinic angle, $\beta = 89.93^\circ$. The monoclinic angle is far too close to 90° for us to be able to resolve it in our neutron powder diffraction experiments, so the material was treated as effectively cubic for most of our analysis.

Neutron diffraction experiments were carried out on the C2 800-wire powder diffractometer (DUALSPEC) at the NRU reactor, Canadian Neutron Beam Centre, Chalk River, Ontario. Temperatures down to 3 K were obtained using a closed-cycle refrigerator. The neutron wavelength was 2.3722(17) Å. The sample consisted of 1.78 grams of fine powder (obtained by hand grinding single crystals down to 3 K) and at 3K (well below $T_N$) allows us to determine $T_N$ and also to look for anomalies that might signal the presence of additional transitions. Figure 2 shows that a simple $J=\frac{1}{2}$ squared Brillouin function fits the temperature dependence of the three peaks very well, yielding an average $T_N$ of 18.0(2) K, consistent with the 17.8 K reported by Mori et al. The fact that $J=\frac{1}{2}$ function works best indicates that the local anisotropy at the Dy sites is strong enough to render the moments essentially Ising-like in DyCd$_6$. Finally, we see no evidence for significant breaks in the behaviour that would indicate additional transitions, in agreement with earlier conclusions based on $C_P$ and $\chi$ data.

Given the weakness of the monoclinic distortion, we evaluated our diffraction patterns in terms of the cubic Im3 structure. At 3 K, we observed strong magnetic contributions at $2\theta = 6.25^\circ$ and 8.85°, indexed as the purely magnetic ($\frac{1}{2} 0 0$ and $100$). To account for these, and other peaks in the magnetic diffraction pattern, within the Im3 space group, we require two propagation vectors to describe the antiferromagnetic order: $k_1 = [0 0 0]$ and $k_2 = [\frac{1}{2} 0 \frac{1}{2}]$, yielding ‘anti-I’ order. We can also describe this same magnetic order in terms of the low-temperature monoclinic group $\text{Ca}_2/c$ ($\#15$) and in this case only a single propagation vector, $k_1 = [1 0 0]$, is required.

In Figure 3 we show Le Bail fits to the 25 K and 3 K neutron powder diffraction patterns of DyCd$_6$. As mentioned above, the effect of the magnetic ordering of the Dy is immediately apparent in the 3 K pattern, especially with the intense, purely magnetic
FIG. 2. Temperature dependence of the three strongest magnetic peaks in Figure 1 fitted with \( J = \frac{1}{2} \) squared Brillouin functions to obtain an ordering temperature of 18.0(2) K.

FIG. 3. Fitted neutron diffraction patterns for DyCd\(_6\) at 25 K (top) and 3.6 K (bottom). The LeBail \(^{13}\) fits demonstrate that long-ranged magnetic order is established and allow us to determine the symmetry of the ordering. Residuals are shown below each fit. Bragg markers for the 3.6 K pattern are (top to bottom) nuclear, magnetic \((\frac{1}{2} 0 \frac{1}{2})\), magnetic \((0 0 0)\).

peaks at \(\theta \sim 6^\circ, 9^\circ, 11^\circ\). At 25 K, the lattice parameter (referred to the cubic cell) is 15.380(1) Å, decreasing slightly to 15.343(1) Å at 3 K. In our analysis, the magnetic and nuclear Bragg peaks shared a common profile function, indicating that the magnetic peaks are resolution limited and that the magnetic order observed here is long-ranged.

The deduced antiferromagnetic structure of DyCd\(_6\) is fully consistent with those reported for TbCd\(_6^{7}\) and HoCd\(_6^{8}\) based on XRMS.

IV. CONCLUSIONS
We have used neutron powder diffraction to show unequivocally that the quasicrystal approximant phase DyCd\(_6\) exhibits long-range antiferromagnetic order below a Néel temperature of 18.0(2) K. The magnetic structure is described by the propagation vectors \( \mathbf{k}_1 = [0 0 0] \) and \( \mathbf{k}_2 = [\frac{1}{2} 0 \frac{1}{2}] \) when referred to the parent cubic \( \text{Im}^3 \) structure, or \( \mathbf{k}_1 = [1 0 0] \) when referred to the low-temperature monoclinic \( C2/c \) structure. Local anisotropy at the Dy sites is strong enough to render the moments essentially Ising-like in DyCd\(_6\).

ACKNOWLEDGMENTS
We are grateful to the staff at CNBC Chalk River for their assistance during the neutron diffraction measurements. Financial support for various stages of this work was provided by the Natural Sciences and Engineering Research Council of Canada and Fonds pour la formation de chercheurs et l’aide à la recherche, Québec. Work done at Ames Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

REFERENCES
1. R. Tamura, Y. Muro, T. Hiroto, K. Nishimoto, and T. Takabatake, Phys. Rev. B 82, 220201 (2010).
2. A. P. Tsai, J. Q. Guo, E. Abe, H. Takakura, and T. I. Sato, Nature (London) 408, 537 (2000).
3. A. I. Goldman, T. Kong, A. Kreyssig, A. Jesche, M. Ramazanoglu, K. W. Dennis, S. L. Bud’ko, and P. C. Canfield, Nature Materials 12, 714 (2013).
4. A. I. Goldman, Sci. Technol. Adv. Mater. 15, 044801 (2014).
5. A. Morii, H. Ota, S. Yoshiuchi, K. Iwakawa, Y. Taga, Y. Hirose, T. Takeuchi, E. Yamamoto, Y. Haga, F. Honda, R. Settai, and Y. Onuki, J. Phys. Soc. Jpn 81, 024720 (2012).
6. R. Tamura, Y. Muro, T. Hiroto, H. Yaguchi, G. Beutier, and T. Takabatake, Phys. Rev. B 85, 014203 (2012).
7. M. G. Kim, G. Beutier, A. Kreyssig, T. Hiroto, J. W. Kim, M. de Boissieu, R. Tamura, and A. I. Goldman, Phys. Rev. B 85, 134442 (2012).
8. A. Kreyssig, G. Beutier, T. Hiroto, M. G. Kim, G. S. Tucker, M. de Boissieu, R. Tamura, and A. I. Goldman, Phil. Mag. Lett. 93, 512 (2013).
9. D. H. Ryan and L. M. D. Cranswick, J. Appl. Cryst. 41, 198 (2008).
10. A. LeBail, P.-F. Lory, R. Flint, T. Kong, T. Hiroto, S. L. Bud’ko, P. C. Canfield, M. de Boissieu, A. Kreyssig, and A. I. Goldman, Phys. Rev. B 95, 054408 (2017).
11. J. Rodríguez-Carvajal, Physica B 192, 55 (1993).
12. T. Roisnel and J. Rodríguez-Carvajal, Mater. Sci. Forum 378-381, 118 (2001).
13. A. LeBail, H. Duroy, and J. L. Fourquet, Mat. Res. Bull. 23, 447 (1988).