A neutron diffraction demonstration of long-range magnetic order in the quasicrystal approximant $DyCd_6$

Cite as: AIP Advances 9, 035312 (2019); doi: 10.1063/1.5079991
Presented: 17 January 2019 • Submitted: 5 November 2018 •
Accepted: 27 November 2018 • Published Online: 11 March 2019

D. H. Ryan,[1,a)] J. M. Cadogan,[2] T. Kong,[3] P. C. Canfield,[3] A. I. Goldman,[3] and A. Kreyssig[3]

AFFILIATIONS

[1]Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada
[2]School of Physical, Environmental and Mathematical Sciences, UNSW Canberra at the Australian Defence Force Academy, BC2610 ACT, Australia
[3]Department of Physics and Astronomy, Iowa State University, Ames, IA 50011, United States

Note: This paper was presented at the 2019 Joint MMM-Intermag Conference.
[a)]**Corresponding author:** D.H. Ryan dhryan@physics.mcgill.ca

ABSTRACT

We have used neutron powder diffraction to demonstrate the existence of long-range antiferromagnetic order of Ising-like Dy moments in the $DyCd_6$ quasicrystal approximant phase. This cubic compound undergoes a slight distortion to a monoclinic cell at low temperatures. The Néel temperature is 18.0(2) K and the magnetic order of the Dy sublattice may be described in the parent cubic $Im\bar{3}$ structure using a combination of two propagation vectors, $\mathbf{k_1} = [0\,0\,0]$ and $\mathbf{k_2} = [\frac{1}{2}\,0\,\frac{1}{2}]$, yielding 'anti-I' order. Alternatively, when referred to the monoclinic $C2/c$ cell, the magnetic structure may be described by a single propagation vector: $\mathbf{k} = [1\,0\,0]$.

I. INTRODUCTION

The cadmium-rich side of most rare-earth (R) cadmium alloy phase diagrams contains RCd_6, a 1/1 cubic approximant based on a *bcc* packing of interpenetrating Tsai-type icosahedral clusters.[1] These clusters are the building blocks of two remarkable families of thermodynamically *stable* binary quasicrystalline rare-earth containing phases: $YbCd_{5.7}$[2] and $RCd_{7.5}$ (R = Gd – Tm, Y)[3] that lie either side of the cubic RCd_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?[4] 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 RCd_6 compounds are quite complex, with most undergoing a structural change from cubic to monoclinic near 170 K[5] and many exhibiting multiple features in heat capacity (C_p) and susceptibility (χ) at much lower temperatures that likely reflect magnetic ordering.[5] Indeed, the sharp nature of the features in C_p and χ[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.[4] The rather large neutron absorption cross-section of natural cadmium has discouraged direct searches for long-ranged magnetic order in the RCd_6 system by neutron diffraction, however x-ray resonant magnetic scattering (XRMS) has been used to demonstrate that both $TbCd_6$[7] and $HoCd_6$[8] adopt long-ranged antiferromagnetic structures below their respective Néel temperatures of 24 K and 8.5 K.

Here we present a neutron powder diffraction study of a $DyCd_6$ sample prepared using natural cadmium and employing a large-area flat-plate technique[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 $TbCd_6$[7] and $HoCd_6$.[8]

II. EXPERIMENTAL METHODS

The $DyCd_6$ sample was prepared at Ames Laboratory using the method outlined by Das *et al.*[10] CuK_α x-ray diffraction confirmed the single-phase nature of the sample with the body-centred cubic $Im\bar{3}$ (#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 $Im\bar{3}$ (#204) at ambient temperatures. Dy occupies the 24g site while Cd occupies several sites (12d, 12e, 16f, 24g (×3) and 48h).[5] It is known that this structure undergoes a slight distortion to a low temperatures monoclinic $C2/c$ (#15) cell with unit cell sides of $\sqrt{2}a_{cubic} \times a_{cubic} \times \sqrt{2}a_{cubic}$ and a monoclinic angle, $\beta = 89.93°$.[6,7]

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 under hexane, to protect from oxidation) spread on a single-crystal silicon plate.[9] All refinements of the neutron diffraction patterns employed the FullProf/WinPlotr package.[11,12] Both elements, Dy and Cd, are strongly neutron-absorbing and this fact, coupled with the effectively cubic symmetry of our powder samples, placed severe limitations on the amount of useful information that could be extracted from a simple neutron powder diffraction experiment. For these reasons, we concentrate herein on our Le Bail[13] ("profile matching") fits to the diffraction patterns since our aim is to present irrefutable evidence for the existence of long-range magnetic order in the $DyCd_6$ quasicrystal approximant.

III. RESULTS AND DISCUSSION

Figure 1 shows the complete diffraction patterns obtained at 25 K (well above T_N) and at 3K (well below T_N) for $DyCd_6$. The two very strong peaks at $50° \le 2\theta \le 60°$ are due to the sample mount. Comparison of the two patterns shows that the magnetic scattering is stronger than the nuclear scattering over a wide angle range. The difference patterns at the bottom of Figure 1 show how extensive the magnetic signal is. Many of the magnetic peaks are clearly at nuclear-forbidden positions suggesting that the magnetic structure breaks the I-centering symmetry of the $Im\bar{3}$ nuclear structure.

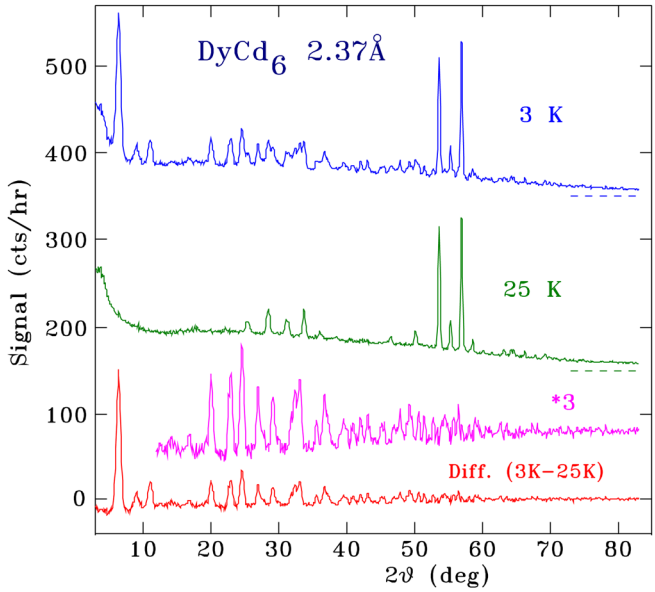

FIG. 1. Neutron diffraction patterns of $DyCd_6$ measured in the magnetically ordered state at 3 K (top, blue) and above the magnetic transition at 25 K (middle, green). Several strong magnetic peaks are evident in the 3 K pattern. The extensive array of magnetic Bragg peaks is emphasised in the difference patterns (bottom, red and magenta) where it is clear that significant magnetic scattering extends past 2θ=60°. The two very strong peaks at $50° \le 2\theta \le 60°$ are due to the sample mount.

Tracking the intensity of the first three (and best isolated) magnetic peaks in Figure 1 at $2\theta \sim 6°$, 9° and 11° 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.*[5] The fact that a $J=\frac{1}{2}$ 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 χ data.[5]

Given the weakness of the monoclinic distortion, we evaluated our diffraction patterns in terms of the cubic $Im\bar{3}$ structure. At 3 K, we observed strong magnetic contributions at $2\theta = 6.25°$ and 8.85°, indexed as the purely magnetic $(\frac{1}{2}\ 0\ \frac{1}{2})$ and (100). To account for these, and other peaks in the magnetic diffraction pattern, within the $Im\bar{3}$ space group, we require two propagation vectors to describe the antiferromagnetic order: $\mathbf{k_1} = [0\ 0\ 0]$ and $\mathbf{k_2} = [\frac{1}{2}\ 0\ \frac{1}{2}]$, yielding 'anti-I' order. We can also describe this same magnetic order in terms of the low-temperature monoclinic group $C2/c$ (#15) and in this case only a single propagation vector, $\mathbf{k_1} = [1\ 0\ 0]$, 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

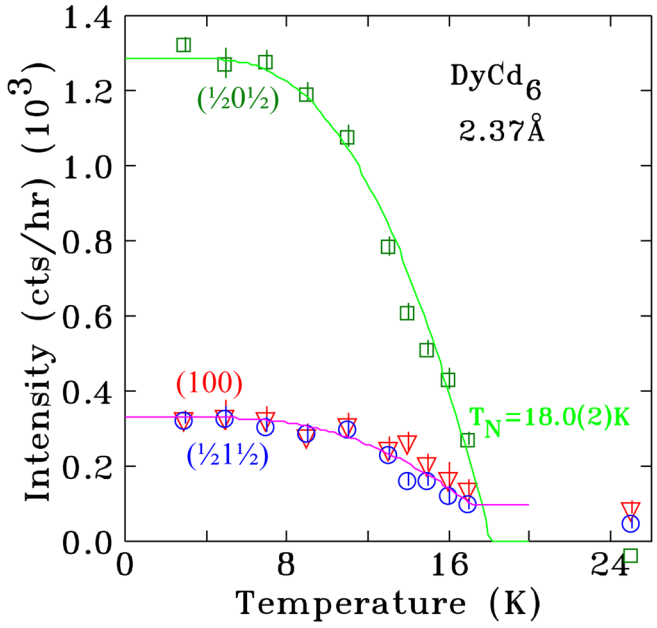

FIG. 2. Temperature dependence of the three strongest magnetic peaks in Figure 1 fitted with J=$\frac{1}{2}$ squared Brillouin functions to obtain an ordering temperature of 18.0(2) K.

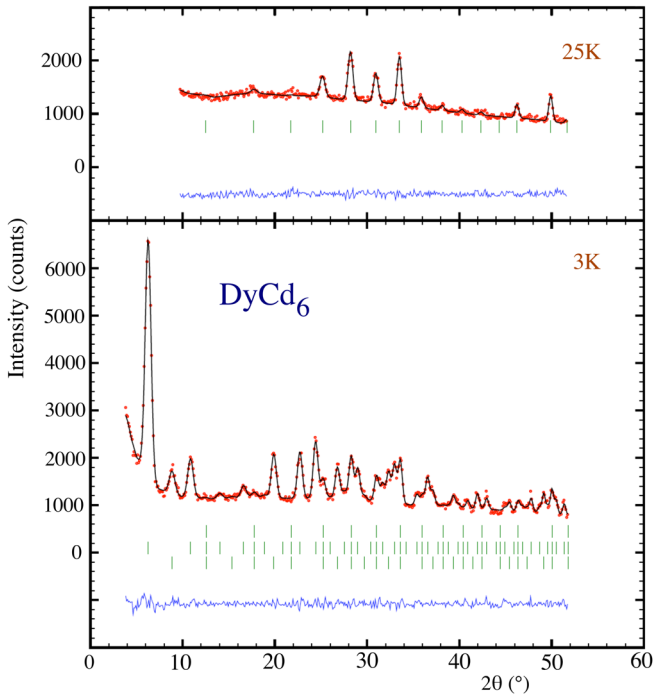

FIG. 3. Fitted neutron diffraction patterns for $DyCd_6$ at 25 K (top) and 3.6 K (bottom). The LeBail[13] fits demonstrate that long-ranged magnetic order is established and allow us to determine the symmetry of the ordering. Residuals are shown below each fit. Bragg markers for the 3.6 K pattern are (top to bottom) nuclear, magnetic ($\mathbf{k_2}$ = [$\frac{1}{2}$ 0 $\frac{1}{2}$]), magnetic ($\mathbf{k_1}$ = [0 0 0]).

peaks at $2\theta \sim 6°, 9°, 11°$. 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 $Im\bar{3}$ 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. J. 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. Mori, 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] P. Das, 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).