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Magnetic structures of rare earth intermetallic compounds $RCuAs_2$ (R = Pr, Nd, Tb, Dy, Ho, and Yb)



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ABSTRACT

Neutron scattering studies have been carried out on polycrystalline samples of a series of rare earth intermetallic compounds RCuAs₂ (R = Pr, Nd, Dy, Tb, Ho and Yb) as a function of temperature to determine the magnetic structures and the order parameters. These compounds crystallize in the ZrCuSi₂ type structure, which is similar to that of the RFeAsO (space group *P4/mmn*) class of iron-based superconductors. PrCuAs₂ develops commensurate magnetic order with $\mathbf{K} = (0, 0, 0.5)$ below $T_N = 6.4(2)$ K, with the ordered moments pointing along the *c*-axis. The irreducible representation analysis shows either a Γ^{1}_{2} or Γ^{1}_{3} representation. NdCuAs₂ and DyCuAs₂ order below $T_N = 3.54(5)$ K and $T_N = 10.1(2)$ K, respectively, with the same ordering wave vector but the moments lying in the *a*-*b* plane (with a Γ^{2}_{9} or Γ^{2}_{10} representation). TbCuAs₂ and HoCuAs₂ exhibit incommensurate magnetic structures below $T_N = 9.44(7)$ and 4.41(2) K, respectively. For TbCuAs₂, two separate magnetic ordering wave vectors are established as $\mathbf{K}_{I(Tb)} = (0.240, 0.155, 0.48)$ and $\mathbf{K}_{2(Tb)} = (0.205, 0.115, 0.28)$, whereas HoCuAs₂ forms a single $\mathbf{K}_{(Ho)} = (0.121, 0.041, 0.376)$ magnetic structure with 3^{rd} order harmonic magnetic peaks. YbCuAs₂ does not exhibit any magnetic Bragg peaks at 1.5 K, while susceptibility measurements indicate an antiferromagnetic-like transition at 4 K, suggesting that either the ordering is not long range in nature or the ordered moment is below the sensitivity limit of $\approx 0.2 \mu_B$.

1. Introduction

Rare earth (R) compounds have generated considerable interest over many decades because of the rich variety of exotic phenomena they display [1], such as unconventional superconductivity [2], coexistence of superconductivity and magnetism [3], multiferroicity [4–6], heavy fermion behaviour [7], and high-T_c superconductivity in cuprates [8]. The most recent exotic phenomenon in rare earth compounds is the hightemperature superconductivity in iron pnictides such as RFeAsO_{1-x}F_x and related systems [9]. The present RCuAs₂ compounds are a new class of rare earth intermetallic materials, which have been the subject of recent studies that have revealed several anomalous properties [10–12]. In these materials, the magnetic properties arise only from the R³⁺ ions, as the Cu¹⁺ ions are non-magnetic (d¹⁰ system). Interestingly, several compounds of RCuAs₂ (R = Tb, Dy, Sm, and Gd) show an anomalous resistivity minimum which happens well above the magnetic phase

transition to long range magnetic order, while others (R = Pr, Nd, Ho, and Yb) do not have such a resistivity minimum even though the magnetic phase transitions are still present. Although the origin of this anomalous resistivity minima is not fully understood, it is believed to be related to the magnetism in these materials. Here we report comprehensive neutron scattering studies of the crystallographic and magnetic properties of the polycrystalline RCuAs₂ (R = Pr, Nd, Dy, Tb, Ho, and Yb) series of compounds. CeCuAs₂ was not considered in these studies as this material shows no evidence of any magnetic order for temperatures down to 45 mK as reported in an earlier work [13]. We confirm that all the measured compounds share the same crystal structure, while the magnetic structures are varied, including both commensurate and incommensurate (IC) antiferromagnetic orderings. Based on the observed magnetic diffraction patterns, we discuss the possible magnetic structures, order parameters, and ordered magnetic moments for this new class of intermetallic compounds.

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2. Experiment details

Polycrystalline RCuAs₂ samples were prepared by employing the solid state synthesis technique. Powders of pure Cu and As and lumps of rare earth metal (purity > 99.5%) were weighed and mixed thoroughly in an argon filled glove box (with H₂O, O₂ < 0.1 µg/g). The mixture was then sealed in evacuated quartz tubes under dynamic vacuum. The ampoules were heated at 900 °C for a week. After an intermediate grinding, additional sintering under the same conditions was performed to obtain homogenous good quality samples. The phase purity of all the samples was checked by powder x-ray diffraction technique using Cu-K_α radiation in the 20 range of 10° to 70° at room temperature. Magnetization measurements in the temperature range from 2 K to 300 K with applied external magnetic field of μ_0 H = 0.5 T were performed on all the samples using a Superconducting Quantum Interference Device (SQUID) magnetometer.

Neutron diffraction experiments were carried out by using the BT1 high-resolution powder diffractometer and BT7 thermal triple-axis spectrometer at National Institute of Standard and Technology (NIST) Center for Neutron Research. All the polycrystalline samples of RCuAs₂ (R = Pr, Nd, Dy, Tb, Ho, and Yb) used for these neutron scattering measurements weighed around 1 g. The samples were sealed in either Aluminium (BT7) or Vanadium (BT1) cans and cooled to the base temperature, which is around 0.4 K-2.5 K depending upon the type of the cryogenics required. For measurements on BT1, the incident neutron wavelength was $\lambda = 1.5397$ Å using the Cu (311) monochromator and collimations of 60'-15' - 7' full-width-at-half-maximum (FWHM) before and after the monochromator and after the sample, respectively. For coarse-resolution/high-intensity diffraction measurements on BT7 the incident neutron wavelength employed was $\lambda = 2.359$ Å and the position sensitive detector (PSD) was placed in the straight-through position to cover around 5° in scattering 2θ angles, taking data in steps of 0.25° and then binning the data to obtain the diffraction pattern [14]. PG filters were employed along the neutron beam path before the monochromator and after the sample to eliminate higher order wavelength contaminations. Unless specified, the collimations used in BT7 measurements were open - 80' - 80' radial (FWHM) along the neutron beam path before and after the monochromator, and after sample, respectively. All the neutron powder diffraction data have been refined using the Rietveld method with software suite FullProf [15]. Representation analysis was carried out using the software SARAh [16] to determine the symmetry-consistent irreducible representations (IRs) of the magnetic structures.

3. Results and discussion

3.1. Crystal structure

All the RCuAs₂ compounds share the same crystal structure (ZrCuSi₂ type with space group P4/nmm) shown in Fig. 1, confirmed by Rietveld refinement results from neutron powder diffraction measurements. We did not observe any indication of structural phase transitions in any of the compounds in the temperature range from room temperature to the lowest measured temperature. Detailed refinement results are listed in Table 1. The crystal structure contains a sequence of layers by means of $As_{(1)} - R - As_{(2)} - Cu - As_{(2)} - R - As_{(1)}$, where $As_{(1)}$ and $As_{(2)}$ are the two inequivalent As-sites, with distorted edge-sharing Cu-As(2) tetrahedral alternating with distorted $As_{(1)}$ -R- $As_{(2)}$ square antiprisms. The sites refined as fully occupied within uncertainties, and in the final fits, the occupancies were fixed at the fully occupied values. These results are consistent with the previously reported x-ray powder diffraction measurements on these materials [17-19]. We did notice that small amounts of impurities (<5%), which are in the form of RAs and/or Cu₃As/Cu₅As₂, exist and were detected by neutron diffraction. However, for the crystal structure refinements, most of the impurity peaks are well separated from the majority phase of RCuAs2 Bragg peaks and can be excluded from the refinement process. In addition, when an Al sample holder was employed



Fig. 1. Crystal structure of RCuAs₂ depicting the edge shared Cu – $As_{(2)}$ tetrahedron and distorted $As_{(1)} - R - As_{(2)}$ square antiprism. The solid (black) box marks the structural unit cell. The figure was created using the VESTA program [22].

Table 1

Summary of the structure refinement results for RCuAs₂ at temperatures above the magnetic phase transition, T_N . All the compounds share the same P4/nnm (# 129) space group, and we did not observe any indication of structural distortions associated with the magnetic transition.

Compounds	$PrCuAs_2$	NdCuAs ₂	TbCuAs ₂	$DyCuAs_2$	$HoCuAs_2$	YbCuAs ₂
Instrument	BT7	BT7	BT1	BT7	BT1	BT7
λ (Å)	2.359	2.359	1.5397	2.359	1.5397	2.359
T (K)	10	10	11	20	4.5	20
a(Å)	3.9806 (3)	3.9534 (4)	3.8818 (1)	3.908 (6)	3.8609 (1)	3.8414 (9)
c(A)	10.065 (1)	10.029 (3)	9.8671 (4)	9.89 (3)	9.7997 (4)	9.729 (9)
R(z) ^a	0.246 (1)	0.241 (1)	0.2394 (5)	0.236 (7)	0.2368 (9)	0.231 (1)
As2(z)	0.3502 (6)	0.346 (1)	0.3381 (5)	0.38 (1)	0.333 (1)	0.332 (2)

^a With R(z) and As2(z) as given above, the full set of the fractional coordinates of all the atoms are: R (R = Pr, Nd, Tb, Dy, Ho, and Yb): (0.25, 0.25, R(z)); As1: (0.75, 0.25, 0.0); As2: (0.75, 0.75, As2(z)); and Cu: (0.75, 0.25, 0.5).

there were Al powder peaks. These peaks are well known and were corefined with the RCuAs_2, and the quoted uncertainties include both effects.

3.2. Commensurate magnetic order in PrCuAs₂, NdCuAs₂, and DyCuAs₂

We start our discussion with the data for PrCuAs₂, NdCuAs₂, and DyCuAs₂, which exhibit simple commensurate magnetic structures. Fig. 2(a) shows representative neutron diffraction data measured on BT7 and Rietveld refinement results for the powder PrCuAs2 sample collected at 0.4 K and 10 K. For unpolarized neutrons the nuclear and magnetic Bragg intensities simply add, and hence the nuclear Bragg peaks are eliminated in the subtraction (assuming a negligible structural distortion associated with the ordering), revealing the magnetic diffraction pattern. Fig. 2(b)–(d) shows the subtracted intensities for PrCuAs₂, NdCuAs₂, and DyCuAs₂, which were collected below and well above the antiferromagnetic ordering temperature for each of these compounds. In the angular range (18° < 2 θ < 53°) shown in Fig. 2b)-d), we find magnetic peaks that can be indexed as the $Q_{mag} = Q_{str} + (0, 0, 0.5)$ in reciprocal lattice units (r. l. u.), where Q_{mag} and Q_{str} are Bragg peak positions for the magnetic and crystal structures, respectively. This establishes the magnetic propagation wave vector **K** as (0, 0, 0.5) for all three compounds. In addition, the systematic absence of the magnetic Bragg peaks at the Q = (0, 0, n + 0.5) positions for PrCuAs₂ (Fig. 2(b), where n = 0, 1, 2 ...,



Fig. 2. (a) Neuron powder diffraction patterns of PrCuAs₂ at T = 0.4 K (blue circles, vertically offset by 1000) and 10 K (green squares) collected on the BT7 instrument. The solid (red) lines are the Rietveld refinement results. The vertical bars are the Bragg Peak positions for (from top to bottom) Al {111} and {200} from sample holder (red), PrCuAs₂ structural (black), and magnetic (blue). (b)–(d) Magnetic (subtracted) diffraction patterns for PrCuAs₂, NdCuAs₂, and DyCuAs₂, respectively. The dashed (green) and solid (red) lines are magnetic diffraction pattern calculations based on two different magnetic models. The vertical bars are the magnetic Bragg peak positions for each of the compounds. The data are plotted against 20 (bottom) and corresponding Q values (top). Error bars in all figures are statistical in origin and represent one standard deviation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

indicates that the magnetic moment direction of the Pr^{3+} is along the *c*-axis, as only the magnetic component perpendicular to the momentum transfer Q can contribute to the magnetic Bragg diffraction intensities. The NdCuAs₂ and DyCuAs₂ data, on the other hand, show strong magnetic peaks at (0, 0, 1.5) (Fig. 2(c) and (d)), indicating that the ordered moment direction is in the *a-b* plane. We remark that it is not possible to determine the spin direction within the plane from powder neutron diffraction due to the tetragonal crystal symmetry. The observed difference in the magnetic moment orientations in these three materials is likely due to the crystal electrical field (CEF) effects.

To solve the magnetic structure, magnetic representation analyses were carried out with the software Sarah [16]. The decomposition of the IRs for the \mathbb{R}^{3+} ions with $\mathbf{K} = (0, 0, 0.5)$ can be written as $\Gamma_{Mag}=\Gamma^1{}_2+\Gamma^1{}_3+\Gamma^2{}_9+\Gamma^2{}_{10}.$ The basis vectors are listed in Table 2 and the illustration for the magnetic structures for each of the IRs is shown in Fig. 3. All four IRs can be considered as bilayer magnetic structures, where within the *a*-*b* plane the spins are aligned ferromagnetically, while the inter-plane interactions are alternating between ferromagnetic and antiferromagnetic depending on going through the R-As(1)-R layers or R-As₍₂₎-Cu-As₍₂₎-R layers. For Γ^{1}_{2} and Γ^{2}_{10} , the antiferromagnetic coupling happens between the R-As_{(1)}-R layers, while R – As_{(2)} – Cu –As_{(2)}- R shows ferromagnetic coupling. In contrast, $\Gamma^1{}_3$ and $\Gamma^2{}_9$ demonstrate exactly the opposite behaviour. In addition, for Γ_2^1 (Fig. 3(a)) and Γ_3^1 (Fig. 3(b)), the ordered magnetic moment directions are along the c-axis, while for Γ^2_{9} (Fig. 3(c)) and Γ^2_{10} (Fig. 3(d)), the ordered moments lie in the *a-b* plane. Since we cannot determine the spin direction within *a-b* plane solely based on the neutron powder diffraction results, for convenience the spin directions were fixed along [110] during the magnetic structure refinement for the Γ^2_{9} and Γ^2_{10} IRs.

Following the above discussion, since the magnetic moments of the Pr ions point along the c-axis, only the $\Gamma^1{}_2$ and $\Gamma^1{}_3$ representations are possible (Fig. 3(a) and (b)). For the Nd and Dy compounds the spins lie in *a-b* plane, so only Γ_{9}^{2} and Γ_{10}^{2} can be the possible options (Fig. 3(c) and (d)). Due to the powder average, Γ_2^1 and Γ_3^1 lead to virtually identical combined diffraction intensities. As a result, it is extremely difficult to distinguish the differences of the calculated diffraction pattern in carrying out the Rietveld refinement process. Even though the Γ_3^1 representation was indicative of slightly better fit for PrCuAs₂, and Γ^2_{10} representation was indicative of slightly better fit for NdCuAs₂, we cannot completely rule out the possibility of the other magnetic structure purely based on the neutron powder diffraction results. The ordered magnetic moments given by the refinements are listed in Table 3 for each possibility. The ordered magnetic moment of \mbox{Pr}^{3+} at 0.4 K is either 1.15(6) $\mu_{\rm B}$ or 1.17(6) $\mu_{\rm B}$ for Γ^1_2 or Γ^1_3 , respectively, which are identical within the uncertainties. Note that the value of the ordered moment is much reduced from the free-ion Pr-ion ordered magnetic moment of 3.2 μ_B (=gJ) [1], indicating that there are significant CEF effects that can

Table 2

Basis vectors (BVs) for the space group P4/nnm (#129) with K = (0, 0, 0.5). The decomposition of the magnetic representation for the R (R = Pr, Nd, and Dy) site, including only non-zero IRs, is $\Gamma_{Mag} = \Gamma_2^1 + \Gamma_3^1 + \Gamma_9^2 + \Gamma_{10}^2$. The atoms of the nonprimitive basis are defined according to 1: (0.25, 0.25, 0.246), 2: (0.75, 0.75, 0.754).

IR	BV At	BV Atom		BV components						
			ma	m_b	m_c	ima	im _b	im _c		
Γ_2	ψ_1	1	0	0	8	0	0	0		
		2	0	0	8	0	0	0		
Γ_3	ψ_2	1	0	0	8	0	0	0		
		2	0	0	-8	0	0	0		
Г9	ψ_3	1	4	0	0	0	0	0		
		2	-4	0	0	0	0	0		
	ψ_4	1	0	-4	0	0	0	0		
		2	0	4	0	0	0	0		
Γ_{10}	ψ_5	1	0	4	0	0	0	0		
		2	0	4	0	0	0	0		
	ψ_6	1	4	0	0	0	0	0		
		2	4	0	0	0	0	0		

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Fig. 3. Illustration of Irreducible representations of RCuAs₂ (only R ions are displayed) with K = (0, 0, 0.5) as (a) Γ^1_2 , (b) Γ^1_3 , (c) Γ^2_9 , and (d) Γ^2_{10} .

Table 3

The refinement results of the ordered magnetic moments based on different IRs for PrCuAs₂, NdCuAs₂, and DyCuAs₂ at the lowest measured temperature.

	$\Gamma_2^1(\mu_{\rm B})$	$\Gamma_3^1(\mu_{\rm B})$	$\Gamma^2_9(\mu_{\rm B})$	$\Gamma^2{}_{10}(\mu_{\rm B})$
Pr (0.4 K)	1.15(6)	1.17(6)	N/A	N/A
Nd (0.4 K)	N/A	N/A	3.2(1)	3.0(1)
Dy (2.5 K)	N/A	N/A	10(1)	10(1)

change the magnetic ground-state from its free-ion 4f-electron configuration. The Nd³⁺ ordered magnetic moments at 0.4 K are 3.2(1) μ_B and 3.0(1) μ_B for Γ^2_9 and Γ^2_{10} , respectively, again the same within the uncertainties. Even though the Nd-ion ordered moments are close to the free-ion values for Nd³⁺ of 3.27 μ_B , the CEF still can have similar magnitude of effects. For DyCuAs₂, both the structure and magnetic Bragg peak intensities are much weaker due to the high absorption crosssection from Dy. Therefore, we can only estimate that the ordered Dy³⁺ magnetic moment at 2.5 K is 10(1) μ_B for either Γ^2_9 or Γ^2_{10} , virtually identical to the free-ion value (10.0 μ_B) [1]. Further information on the magnetic models will require single crystal neutron diffraction measurements if high quality single crystal samples become available in the future.

Fig. 4 shows measurements of the integrated magnetic Bragg peak intensities, proportional to the square of the antiferromagnetic order parameter (sublattice magnetization), at (1, 0, 0.5) for PrCuAs₂ and (0, 0, 0.5)



Fig. 4. Temperature dependence of the integrated magnetic Bragg peak intensities of (a) PrCuAs₂, (b) NdCuAs₂, and (c) DyCuAs₂. The solid (orange) curves show the mean field order parameter fit results for each of these compounds. The vertical dashed (red) lines indicate the fitted $T_N = 6.4(2)$ K for PrCuAs₂, $T_N = 3.54(5)$ K for the NdCuAs₂, and $T_N = 10.1(2)$ K for the DyCuAs₂. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1.5) for NdCuAs₂ and DyCuAs₂, respectively. The temperatureindependent data collected well above the Néel temperatures (T_N) were used as background and subtracted from the data. The integrated intensities for each material smoothly emerge as the temperature drops below the T_N, indicating that the magnetic transition is 2nd order in nature. The solid curves shown in Fig. 4 (a)–(c) are simple fits using mean field theory to fit the intensities, which are proportional to the square of the ordered magnetic moment. The fits give T_N = 6.4(2) K for PrCuAs₂, T_N = 3.54(5) K for NdCuAs₂, and T_N = 10.1(2) K for DyCuAs₂. The above results are in very good agreement with the bulk magnetic property measurements reported previously [10,11] and in this work as well (not shown).

3.3. Incommensurate magnetic order in TbCuAs₂ and HoCuAs₂

Fig. 5 shows the structure and magnetic diffraction pattern of TbCuAs₂ and HoCuAs₂ measured with the BT1 diffractometer. It is clear that the patterns are considerably more complicated than for the previous materials, with many magnetic Bragg peaks. None of these new Bragg peaks could be indexed with commensurate propagation wave vectors, clearly indicating that the magnetic structures are incommensurate. Using the K-search program from FullProf suite, we cannot find a unique K-vector for the Tb compound. In particular, the double magnetic peaks near 8° (0.55 and 0.60 Å⁻¹) and 16° (1.07 and 1.16 Å⁻¹) shown in Fig. 5(b) preclude any possible solution for a single K-vector. After an extensive search, we found two IC magnetic ordering K-vectors for Tb as $K_{1(\text{Tb})} = (0.240, 0.155, 0.48)$ and $K_{2(\text{Tb})} = (0.205, 0.115, 0.28)$. The magnetic peaks of TbCuAs₂ (Fig. 5(b)) then can be indexed as 0.55 Å⁻¹: $(000) + K_1, 0.60 \text{ Å}^{-1}: (001) - K_2, 1.07 \text{ Å}^{-1}: (002) - K_1, 1.16 \text{ Å}^{-1}: (002) - K_2, 1.07 \text{ Å}^{-1}: (002$ K_2 , 1.46 Å⁻¹: (011) – K_1 . For the Ho system, on the other hand, we obtain the unique result of $K_{(Ho)} = (0.121, 0.041, 0.376)$, together with third order harmonics (i.e. 3^*K). The HoCuAs₂ magnetic peaks (Fig. 5(d)) then can be indexed as 0.31 Å⁻¹: (000) + **K**, 0.84 Å⁻¹: (002) - 3***K**, 0.91 Å⁻¹: (001) + K, 0.94 Å⁻¹: (000) +3*K, 1.20 Å⁻¹: (102) - 3*K. The above Kvalues explain the observed peak positions, with all three components being incommensurate indicating a very complex magnetic structure. For any choices, however, the calculated magnetic scattering intensities cannot reproduce the observed magnetic Bragg peak intensities within the uncertainties with either a simple sine wave, helix or square wave models. Even with arbitrary components of the magnetic moments, we were not able to obtain a completely satisfactory solution for the magnetic structure. Further progress in this work will likely require high quality single crystal measurements.

Fig. 6 shows the order parameter measurements for the strongest magnetic peaks of TbCuAs $_2$ and HoCuAs $_2$, measured on BT7. The

integrated intensities of these strong fundamental magnetic Bragg peaks evolve smoothly and continuously with temperature, indicating that the magnetic phase transition is 2nd order in nature. Mean-field fits of the magnetic Bragg peak intensities give $T_N = 9.44(7)$ K for TbCuAs₂ and $T_N = 4.41(2)$ K for HoCuAs₂, respectively. Fig. 7 shows a colour map of this peak as a function of temperature for HoCuAs₂, taken using an energy analyser and Söller collimations of 25' before and after the sample. We see that the scattering evolves smoothly with temperature without any significant broadening. More importantly, there is no significant variation in the position of the peak, so that the incommensurate wave vector does not vary significantly with temperature.

3.4. Absence of long range magnetic order in YbCuAs₂

Fig. 8(a) shows the magnetic susceptibility measurements for the YbCuAs₂ powder sample, which are similar to those reported previously [10]. This result is indicative of an antiferromagnetic phase transition below $T_N = 4$ K. However, as seen in Fig. 8(b), the neutron powder diffraction measurements of the YbCuAs₂ sample on BT7 did not show any additional Bragg peaks at T = 1.5 K, well below the presumed $T_N = 4$ K. Absence of any magnetic Bragg peak indicates either there is no long range magnetic order down to 1.5 K, or the ordered magnetic moment of Yb ions is smaller than our current experimental limit, ≈ 0.2 $\mu_{\rm B}$. It is noteworthy that the authors in Ref. [10] expressed their surprise on the relatively high magnetic ordering temperature of the Ybcompound. Our neutron powder diffraction results could indicate the possibility that the anomalies in resistivity and magnetic susceptibility measurements in YbCuAs₂ are related to something else other than the long range magnetic order, as for example, moment instability. There are examples of Yb-compounds where Yb-ions have nearly the theoretical paramagnetic moment but at low temperature the Yb-ions are nonmagnetic, for example in, $YbMCu_4$ (M = Ag and In) [20,21]. We



Fig. 5. (a) High resolution neutron powder diffraction pattern taken on BT1 of TbCuAs₂ measured at T = 2.5 K (blue closed circles, vertically offset by 1000) and 11 K (open green squares). (b) Subtracted (magnetic) diffraction pattern of TbCuAs₂. (c) High resolution neutron powder diffraction pattern of HoCuAs₂ measured at T = 1.5 K (blue closed circles, vertically offset by 1000) and 4.6 K (open green squares). (d) Subtracted (magnetic) diffraction pattern of HoCuAs₂. The solid (red) lines in (a) and (c) are the Rietveld structure refinement results for TbCuAs₂ and HoCuAs₂, respectively. The (red) "*" marks the Al powder peaks from the sample holder with $2\theta \approx 44.9^{\circ}$ and 65.3° . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Temperature dependence of the integrated magnetic Bragg peak intensities of (a) TbCuAs₂ and (b) HoCuAs₂, respectively, for two different first-order peaks. The intensities have been scaled to demonstrate that they obey the same temperature dependence. The represented magnetic Bragg peaks occur in (a) TbCuAs₂ at Q around 1.16 Å⁻¹ (closed circles) and 1.46 Å⁻¹ (open squares), and in (b) HoCuAs₂ at Q around 0.31 Å⁻¹ (closed circles) and 0.91 Å⁻¹ (open squares), respectively. The solid (orange) curves show the mean field order parameter fit results for each compound. The vertical dashed (red) lines indicate the fitted $T_N = 9.44(7)$ K for (a) TbCuAs₂, and $T_N = 4.41(2)$ K for (b) HoCuAs₂, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

suspect a similar situation may occur in YbCuAs₂. Investigations using Mössbauer or μ SR techniques might be helpful to clarify this situation, or again if single crystals of sufficient size become available diffraction measurements with more sensitivity could be carried out.

4. Crystal field effects

The ordered magnetic moments that are well below the free-ion values for some of these materials, the different magnetic moment directions, and incommensurate magnetic structures for others all suggest that crystal field effects are likely important for these rare-earth systems. Consequently, we have carried out inelastic neutron scattering measurements on the Pr, Tb, Ho, and Yb samples to search for crystal electric field (CEF) excitations. The particular aim for these measurements was to determine if there are low-lying CEF states that would be thermally populated near and below T_N and affect the occupancy of the ground state CEF level and thereby the behaviour in ordered state, or in the case of Yb result in a non-magnetic ground state. For these measurements, we employed the BT7 instrument using horizontal focusing of the analyser (since CEF excitations are dispersionless) with a fixed final energy $E_f = 14.7$ meV, with a PG filter in the scattered beam path to suppress higher order contaminations. The collimation employed was 80' before (open position) and after the monochromator, an 80'-radial collimator before the analyser, and no collimation after. The measured energy



Fig. 7. Contour map of the magnetic Bragg peak intensity as a function of temperature at a scattering angle around 6.7° for HoCuAs₂. For these low-angle measurements we employed an energy analyser and tighter collimation to improve the signal to noise. The background scattering at high temperature has been subtracted. Note that there is no significant change in the wave vector of the incommensurate order, nor is there significant broadening of the scattering in the vicinity of the phase transition.



Fig. 8. (a)Plot of low temperature susceptibility (black squares) for YbCuAs₂ and its inverse measured (blue circles) with an applied external magnetic field of $\mu_0H = 0.5$ T. The peak in the susceptibility at 4 K indicates the magnetic phase transition (T_N). (Note that 1 emu/(mol·Oe) = $4\pi \times 10^{-6}$ m³/mol). (b) Diffraction pattern at 1.5 K (blue circles, vertically offset by 1000) and 20 K (green squares). The diamond (red) shows the intensity difference between 1.5 K and 20 K, which does not reveal any magnetic Bragg peaks. The solid (black) lines are the structure refinement results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

resolution at the elastic position then was 1.4 meV FWHM. Energy transfers were measured from the elastic position up to 30 meV at a number of Q positions within the range from 2.35 Å⁻¹ to 3.5 Å⁻¹ for selected temperatures above T_N. However, we could not identify any CEF excitations in this energy range for any of the measured samples. This suggests that either the observable CEF levels occur above 30 meV, or they are too broad to be observed. There could also be CEF levels at low energies within the instrumental resolution, in the range below ~0.5 meV, but it is unlikely that all the CEF levels are in this range for all the materials investigated. These results are in contrast to the previous theoretical predictions of CEF excitations [12], for example the predicted three low-lying state for Tb ions at 2.62, 2.96, and 6.25 meV above the ground state.

5. Conclusion

We have carried out systematic neutron diffraction studies on the intermetallic polycrystalline samples of $RCuAs_2$ with R = Pr, Nd, Dy, Tb, Ho, and Yb. We observed long range magnetic order in all the compounds except YbCuAs₂, with Néel temperatures of 10 K or below. As inferred from the temperature dependence of the order parameters, the magnetic phase transition are all continuous (second-order) in nature within the uncertainties of the measurements. We have successfully solved the magnetic structures for the PrCuAs₂, NdCuAs₂, and DyCuAs₂, which all have the same *commensurate* ordering wave-vector K = (0, 0, 0.5). For PrCuAs₂, the magnetic moments are parallel to the crystal c-axis, whereas in NdCuAs₂ and DyCuAs₂ the magnetic moments lie in the a-b plane. In addition, the ordered magnetic moment for PrCuAs₂ is much reduced from the free-ion value, while for NdCuAs₂ and DyCuAs₂, the ordered magnetic moments are close to their free-ions values. These differences in the magnetic moment orientation as well as the value of the ordered moments likely originates from the CEF effects. The TbCuAs2 and HoCuAs₂ systems have much more complicated incommensurate magnetic structures. The ordering wave-vectors for TbCuAs₂ are (0.240,0.155,0.48) and (0.205, 0.115, 0.28), while for HoCuAs₂ there is a unique ordering vector of (0.121, 0.041, 0.376) with the 3rd order harmonics. Nevertheless, the magnetic structure refinement using the above IC wave-vectors cannot fully reproduce the intensities of the magnetic Bragg peaks and consequently a complete solution to the magnetic structures has not been obtained. Considering the complexity of the neutron powder diffraction data, measurements on high quality single crystals become essential for the determination of possible magnetic models for TbCuAs₂ and HoCuAs₂. The absence of any clear magnetic Bragg peaks in YbCuAs₂ implies no long range magnetic ordering down to 1.5 K, or an ordered below the limit of 0.2 μ B. One possibility is that the Yb CEF ground state is non-magnetic. We were not able to detect any crystal field levels for any of these materials in the energy range from \sim 0.5 meV to 30 meV, indicating that the levels are too broad to observe or lie at higher/lower energies. Further neutron studies on single crystals of these materials would be helpful to clarify certain details of the magnetic structures and the associated spin dynamics.

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