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Quasicrystal approximant $\text{Ho}_{13}\text{Zn}_{58}$: an incommensurate modulated tunnel structure

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Abstract

In a systematic study of the binary quasicrystal approximants $RE_{13}Zn_{58}$ (RE =rare earth elements) system, single crystals of $\text{Ho}_{13}\text{Zn}_{58}$ have been prepared. It is unique among the family members of the $RE_{13}Zn_{58}$ system, in that it shows a modulated superstructure ordering. Satellite reflections observed in single crystal X-ray diffraction pattern indicate the presence of a one-dimensional lattice distortion. The modulated structure has been solved and refined from X-ray data using the superspace group approach. The $\text{Ho}_{13}\text{Zn}_{58}$ structure can be described in the (3+1)-dimensional superspace group $Pc2_1n (0\beta 0)s0s$ with lattice parameters $a=24.6481(7)\text{\AA}$, $b=14.2484(4)\text{\AA}$, $c=14.0153(3)\text{\AA}$ and a modulation vector $q=(0, 0.741, 0)$. The crystal structure is closely related to those of the other $RE_{13}Zn_{58}$ compounds, comprising hexagon-shaped tunnels, made up of rare earth centred Zn polyhedra. All atoms in the structure are affected by a displacive modulation but one set of Zn atoms are very strongly affected, and display an almost composite behaviour with regard to the rest of the structure.

1. Introduction

M. Armbrüster and S. Lidin reported the reassessment of the approximant CeCd_6 to $\text{Ce}_6\text{Cd}_{37}$ [1] in 2000 and revealed a previously unreported order in the central tetrahedron and prompted the re-examination of the structures in the $RE\text{Cd}_6$ system. C. P. Gómez and S. Y. Piao et al. have extensively studied some of the $RE\text{Cd}_6$ approximants in the rare earth–cadmium system [2,3] and found different types of disorder with the central tetrahedra located in the dodecahedral cavities. The recent report of stable icosahedral quasicrystals in the $RE\text{-Cd}$ systems [4,5,6] together with the elucidation of the complex order-disorder behaviour of the cubic approximants [2,3,7,8,9,10] has aroused a renewed interest for more detailed understanding of the related hexagonal 13:58 phases. From studies of the Dy-Zn systems [11], it is apparent that the 13:58 phases indeed show similar complexity to the $RE\text{Cd}_6$ system and both systems are structurally related to each other and can to a certain extent be described by the same structural building blocks.

We have investigated most of the $RE_{13}Zn_{58}$ quasicrystal approximants ($RE = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Lu) by the single-crystal x-ray diffraction method. The crystal structures are generally rather more complex than previously reported [12,13,14] and exhibit a number of different ordering modes. Basically the structures can be divided into two systems; hexagonal ones and orthorhombic ones. In a previous work [15], we reported on the hexagonal structures formed by Zn together with larger rare earths; Ce, Pr, Nd, Sm, Gd, Tb and Dy. The orthorhombic structures formed together with the smaller elements in the rare earth family such as Ho, Er, Tm and Lu show much more complex behaviour. $\text{Ho}_{13}\text{Zn}_{58}$ is unique among the family members of the $RE_{13}Zn_{58}$ system, in that it shows a modulated superstructure ordering.

2. Experimental

Syntheses and Characterization

The Ho chips and Zn metal (splinters from a rod of pure metal) were mixed in niobium ampoules and sealed under argon. Several different annealing temperatures and compositions $RE : Zn$ were tried to optimize the yield of the target phase due to the paucity of pertinent information. The single crystal prepared for the data collection was obtained from the sample which was annealed for a period of 48 hours at about 835 K. After annealing, the furnace was turned off with the samples left inside to cool down to ambient temperature (initial cooling rate 3 °C/min). All preparations were carried out in an argon atmosphere in order to avoid detrimental effects from water vapour or oxygen. Elemental impurity levels in the samples were below the detection limit of Energy Dispersive X-ray analysis.

X-ray data collection and refinement

The single-crystal data was collected on an Oxford Diffraction Xcalibur CCD diffractometer with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) operated at 50 kV and 40 mA. The crystal to detector distance was 80 mm. The intensities of the reflections were integrated using the machine specific software. Energy dispersive X-ray analysis was carried out using a JEOL 820 scanning electron microscope at 20 kV accelerating voltage with a Si detector LINK AN10 000. Corrections were made for atomic number, absorption, and fluorescence. EDX analysis was performed on approximately six different crystals from each synthesized sample in order to ascertain the elemental purity. Due to the irregular shape of the crystals, absorption correction on such a crystal by the actual measurement of the shape is inapplicable. Therefore, a numerical absorption correction, based on a shape obtained by optimizing the equivalence for symmetry related reflection, was performed with the programs X-RED [16] and X-SHAPE [17]. The refinement of the structure was performed using the program JANA2000 [18]. The images were rendered using the program DIAMOND [19], version 2.1c.

A detailed description of the crystal data, data collection and refinement were given in Table I.

3. Symmetry determination and structure model

The archetype structure is that of $Ce_{13}Zn_{58}$, with the space group symmetry $P6_3/mmc$, and so a group-subgroup relation is expected to exist between the symmetry of the basic structure of $Ho_{13}Zn_{58}$ and $P6_3/mmc$. Two distinct sets of superstructure reflections are clearly discernable in the reciprocal lattice images of $Ho_{13}Zn_{58}$ (conf. Fig.1); the first being the standard doubling of the hexagonal a , and b axes. From experience with previous examples in this structural family, it is expected that only one direction is actually doubled, and the rest of these reflection appear as a result of twinning. This is further corroborated by the uneven intensity distribution between the twin individuals, indicating strongly unbalanced twinning of orthorhombic super cell. A further set of super structure reflections occur along the orthorhombic b -axis. They are metrically close to a fourfold super structure ($q \approx 0, \frac{1}{4}, 0$), but the intensity distribution is strongly indicative of a modulated behaviour. Further, strong satellites appear close to weak reflections, and *vice versa*. This is taken to indicate that the q vector should be chosen as $q \approx (0, \frac{3}{4}, 0)$. Symmetry-wise, the doubling of one axis corresponds to first breaking the hexagonal symmetry, and then the C-centring of the orthorhombic sub cell, in the sequence $P6_3/mmc - Ccmm - (Pcmm, Pcmn, Pnmm, Pnmm, Pcam, Pcan, Pnam, Pnan)$

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4 The remaining systematic absences in the diffraction pattern include the conditions $0kl$,
5 $l=2n+1$ absent for main reflections and $hk0$, $h+k=2n+1$ absent for main reflections. This
6 strongly suggests that $Pcmn$ is the correct 3d space group for the main structure. Inspecting
7 satellite reflections yields more information. The condition $0kl$, $l=2n+1$ absent expands to
8 $Oklm$, $l+m=2n+1$ absent while $hk0$, $h+k=2n+1$ absent becomes $hk0m$, $h+k+m=2n+1$ absent,
9 that is, for both sets of reflections, allowed main reflections do not show satellites, while those
10 forbidden by the extinction conditions do. This unambiguously shows that the maximal
11 allowable superspace group for $\text{Ho}_{13}\text{Zn}_{58}$ is $Pcmn(0\beta 0)s0s$ with $\beta \approx \frac{3}{4}$.
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15 A model was constructed by first reducing the symmetry of the $P6_3/mmc$ type $\text{Ce}_{13}\text{Zn}_{58}$
16 structure (conf. Fig. 2) to $Pcmn$, and refining this against main reflections. The cause of the
17 modulation becomes quite obvious, since a sine-wave shaped electron density permeates the
18 structure along the orthorhombic b direction (conf. fig. 3). This phenomenon is also observed
19 in $\text{Er}_{13}\text{Zn}_{58}$, $\text{Tm}_{13}\text{Zn}_{58}$ and $\text{Lu}_{13}\text{Zn}_{58}$. In the Ho case, it appears however that the phenomenon
20 is more ordered, and the electron density of the sine-wave was modelled using a large number
21 of isotropic atomic (Zn) positions. After convergence, those Zn atoms were allowed
22 sinusoidal occupational modulations, leading to some reduction of R -values for satellites. The
23 model was however quite unsatisfactory at this stage. A reduction in symmetry to the non
24 centric group $Pc2_1n$ produced a major reduction in residuals, and the rest of the structure was
25 then allowed to relax according to the modulation. Inspection of the model thus constructed
26 showed very strong occupational modulations for the atoms modelling the sinusoidal electron
27 density, and the harmonic modulation waves were replaced by occupational square waves.
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33 4. Results and outlook

34 It is clear that the structure is not fully ordered, but that the mechanism for the modulation is
35 straight-forward; the sinusoidal electron density delineates a channel wherein interstitial Zn
36 atoms are accommodated. The interactions between the Zn atoms within this channel are
37 substantially stronger than those between Zn in the channel and the surrounding structure.
38 This leads to a displace motion of Zn-atoms in the tube with respect to the surrounding basic
39 structure. The structure may therefore more appropriately be described as a composite, but the
40 modelling of this is rather complex and we here present the structure as modelled in a classic,
41 modulated fashion. The fact that the structures of the corresponding Er, Tm and Lu structures
42 show the same disorder (albeit without satellites) may indicate that the modulation may be
43 tuned in a ternary compound to yield more ordered structures.
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45

46 There is a nice correspondence between the $\text{Ho}_{13}\text{Zn}_{58}$ structure and the cubic approximants:
47 The disordered electron density of the sine wave passes through the space diagonal of the
48 small Zn_8 cubes formed between the larger HoZn_{16} polyhedra. This behaviour mimics that in
49 the cubic phases where partial occupancy of the Zn_8 cubes leads to extended electron density
50 along the $\langle 111 \rangle$ directions of the unit cell.
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52

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55 Strategic Research are gratefully acknowledged.
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Table I. Crystal data, data collection and refinement parameters for the structures

Crystal data	
Chemical formula	$\text{Ho}_{13}\text{Zn}_{58.6}$
Formula weight (g/mol)	5936.1
Temperature of measurement (K)	293
Super space group	$Pc2_1n(0\beta 0)s0s$
a (Å)	24.6481(7)
b (Å)	14.2484(4)
c (Å)	14.0153(3)
Modulation wave vector q	$0.741 b^*$
Z	4
$F(000)$	10504
Calculated density (g/cm ³)	8.008
Absorption coefficient (mm ⁻¹)	48.222
T_{\min}, T_{\max}	0.0413, 0.2432
Data collection	
Diffractometer	Xcalibur CCD diffractometer
No. of image	3027
Number of measured reflections	36862
Number of independent reflections	18977
Number of observed reflections	7887
Number of main reflections	3639
Number of satellites	1104
R_{int} (obs/all) (%)	0.0380, 0.0509
Refinement	
R_{all} (R, wR)	0.0478, 0.0552
R_{main} (R, wR)	0.0363, 0.0436
$R_{\text{satellite}}$ (R, wR), 1st order	0.1579, 0.1687
Number of parameters	728
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e/Å ³)	3.77, -4.76
Absorption correction	Numerical From shape

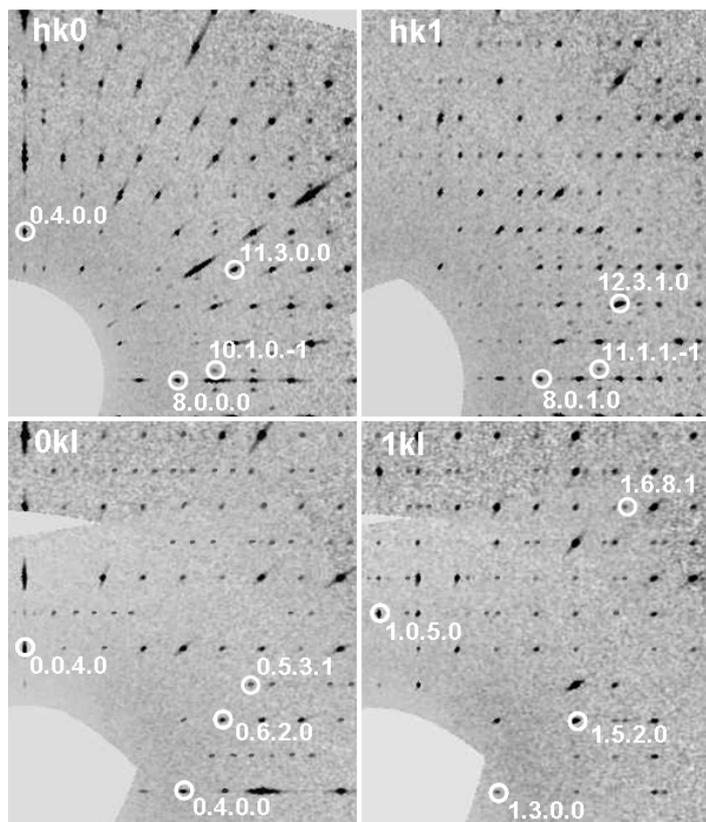


Fig. 1. The reciprocal planes of $\text{Ho}_{13}\text{Zn}_{58}$, extracted from single crystal x-ray diffraction raw data, indices referring to the orthorhombic cell. Note the systematic absences in the zero order zones.

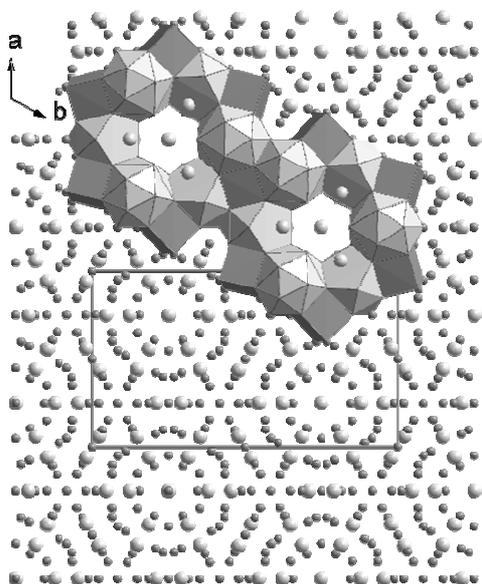


Fig. 2. The crystal structure of $\text{Ce}_{13}\text{Zn}_{58}$ is projected down the corresponding $[001]_h$ direction of the basic hexagonal type structure. Light and dark grey spheres represent Ce and Zn atoms respectively. The orthorhombic unit cell is drawn for convenient comparison to the orthorhombic $\text{Ho}_{13}\text{Zn}_{58}$ compound.

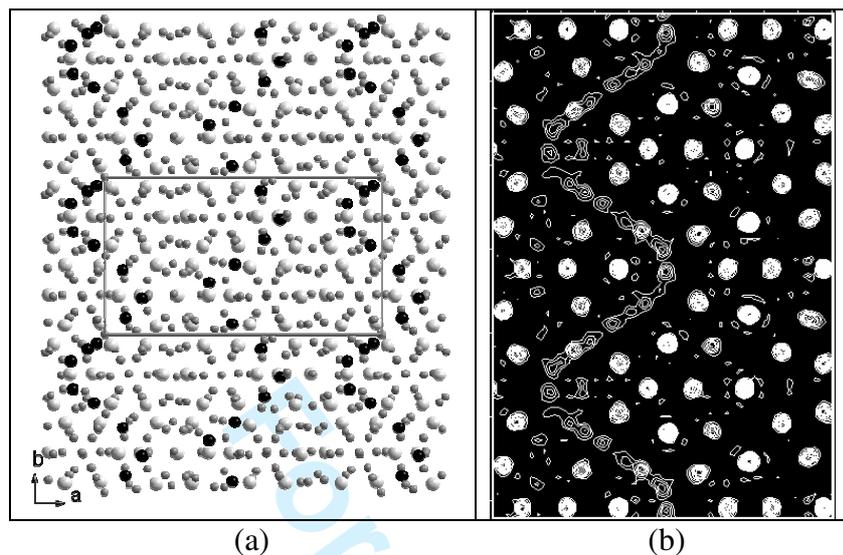


Fig. 3. (a) The crystal structure of $\text{Ho}_{13}\text{Zn}_{58}$ projected down the direction corresponding to $[001]_h$ of the basic hexagonal type structure. Light and dark grey spheres represent Ho and Zn atoms respectively. The black spheres represent Zn atoms on the beads-on-a-string like chain. (b) The beads-on-a-string like electron density map (calculated from F_{obs}) showing the disorder behaviour of some Zn atoms in the $\text{Ho}_{13}\text{Zn}_{58}$ compound.