Orthorhombic charge density wave on the tetragonal lattice of EuAl₄

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Charge density wave, Twinning, Modulated, Superspace

Abstract
EuAl$_4$ possesses the BaAl$_4$ crystal structure type with tetragonal symmetry $I4/mmm$. It undergoes a charge-density-wave (CDW) transition at $T_{CDW} = 145$ K and it features four consecutive antiferromagnetic phase transitions below 16 K. Here, we use single-crystal x-ray diffraction to determine incommensurately modulated crystal structure of EuAl$_4$ in its CDW state. The CDW is shown to be incommensurate with modulation wave vector $\mathbf{q} = (0, 0, 0.1781(3))$ at 70 K. The symmetry of the incommensurately modulated crystal structure is orthorhombic with superspace group $Fmmm(00\sigma)s00$, where $Fmmm$ is a subgroup of $I4/mmm$ of index 2. Both the lattice and the atomic coordinates of the basic structure remain tetragonal. Symmetry breaking is entirely due to the modulation wave, where atoms Eu and Al1 have displacements exclusively along $a$, while the fourfold rotation would require equal displacement amplitudes along $a$ and $b$. The calculated band structure of the basic structure and interatomic distances in the modulated crystal structure both indicate the aluminum atoms as location of the CDW. The temperature dependence of the specific heat reveals an anomaly at $T_{CDW} = 145$ K of a magnitude similar to canonical CDW systems. The present discovery of orthorhombic symmetry for the CDW state of EuAl$_4$ leads to the suggestion of monoclinic instead of orthorhombic symmetry for the third AFM state.

1. Introduction

EuAl$_4$ has attracted attention, because it develops a charge-density wave (CDW) below $T_{CDW} = 145.1$ K and it exhibits four successive magnetic transitions below 16 K (Nakamura et al., 2015; Shimomura et al., 2019). EuAl$_4$ adopts the BaAl$_4$ structure type that has symmetry according to the tetragonal space group $I4/mmm$ (Parthé et al., 1983; Nakamura et al., 2015), as shown in Fig. 1. It belongs to a large family of isostructural compounds, including magnetic EuGa$_4$, fully ordered EuAl$_2$Ga$_2$ and
non-magnetic SrAl$_4$ and BaAl$_4$ (Nakamura et al., 2016; Stavina et al., 2018; Onuki et al., 2020). Recently, a symmetry-protected non-trivial topology of the electronic band structure was proposed for BaAl$_4$ (Wang et al., 2021). In case of magnetic EuAl$_4$, a chiral spin structure, like skyrmions reported in some divalent Eu compounds such as EuPtSi (Kaneko et al., 2019; Onuki et al., 2020), was proposed on the basis of the observation of the topological Hall resistivity and muon-spin rotation and relaxation ($\mu$SR) studies (Shang et al., 2021; Zhu et al., 2022). If such a nontrivial texture would be confirmed, EuAl$_4$ would represent a rare case of a compound where one could observe the coexistence of exotic magnetic order and a CDW. Since these exotic electronic and spin structures depend on the symmetry, knowledge of the true symmetry of the crystal structure thus is of utmost importance for understanding non-trivial magnetic properties. Here we show that the CDW transition of EuAl$_4$ is accompanied by a lowering of the symmetry towards orthorhombic, and we present the incommensurately modulated CDW crystal structure.

EuAl$_4$ is one of a few compounds (Schutte et al., 1993), where the lowering of the crystal symmetry at a phase transition is governed by the symmetry of the incommensurate modulation wave describing the CDW, while any lattice distortion could not be detected in the present high-resolution diffraction experiment with synchrotron radiation. This feature might explain why the lowering of symmetry has not been found in earlier studies on EuAl$_4$. This behavior is in contrast to other CDW materials, like Er$_2$Ir$_3$Si$_5$, Lu$_2$Ir$_3$Si$_5$ and BaFe$_2$Al$_9$, for which the CDW transitions are accompanied by large lattice distortions (Ramakrishnan et al., 2020; Ramakrishnan et al., 2021; Meier et al., 2021).

The phenomenon of CDW was originally identified as a property of crystals with quasi-one-dimensional (1D) electron bands, such as NbSe$_3$ and K$_{0.3}$MoO$_3$ (Gruner, 1994; Monceau, 2012). A CDW is formed due to Fermi surface nesting (FSN), where
the nesting vector of the periodic structure becomes the wave vector of the CDW of the metallic bands as well as of the accompanying modulation of the atomic positions (periodic lattice distortion—PLD). The modulation wave vector can be commensurate or incommensurate with respect to the underlying periodic basic structure. More recent research has found that CDWs can develop in crystalline materials that lack the 1D property of their crystal structures and rather possess three-dimensionally (3D) structured electron bands. Alternate mechanisms have been proposed for the formation of CDWs in 3D compounds, including the mechanism of $q$-dependent electron-phonon coupling (EPC) (Zhu et al., 2015; Zhu et al., 2017). Strongly correlated electron systems may also support the formation of CDWs (Chen et al., 2016). The latter are often found for rare-earth containing intermetallic compounds, like the series of isostructural compounds $R_5\text{Ir}_4\text{Si}_{10}$ ($R =$ rare earth) (Ramakrishnan & van Smaalen, 2017).

The interplay between CDWs and magnetism in rare-earth compounds continues to attract attention. A competition between these two symmetry-breaking phenomena can be expected, because both CDWs and magnetic order depend on the Fermi surface through FSN and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between the localized magnetic moments of the $4f$ electrons, as it is found for EuAl$_4$ (Kobata et al., 2016). In case of magnetoelastic coupling, the lattice distortion may couple to the PLD or the lattice distortion in the CDW state or to the EPC. Experimentally, the coexistence of a CDW and antiferromagnetic (AFM) order has been established for Er$_5\text{Ir}_4\text{Si}_{10}$ and Sm$_2\text{Ru}_3\text{Ge}_5$ (Galli et al., 2002; Kuo et al., 2020). The series of compounds $R\text{NiC}_2$ ($R =$ Pr, Nd, Gd, Tb, Dy, Ho, Er) exhibit both CDW and AFM phase transitions (Roman et al., 2018; Shimomura et al., 2016; Kolincio et al., 2017; Maeda et al., 2019). SmNiC$_2$ is an exception in this series, since it develops ferromagnetic (FM) order below $T_C = 17.7 \text{K}$ at which transition the CDW is destroyed (Shimomura et al., 2009; Wöllfel et al., 2010). Recently, coexistence of CDW and FM orders was
found for the field-induced FM state of TmNiC$_2$ (Kolincio et al., 2020).

Magnetism of EuAl$_4$ is related to localized magnetic moments of the europium atoms in their divalent state: the electronic configuration $4f^7$ implies $J = S = 7/2$ and $L = 0$, where $J$ is the total angular momentum, $S$ is the spin angular momentum and $L$ is the orbital angular momentum (Wernick et al., 1967; Nakamura et al., 2015). This allows the study of the collective magnetism without single-ion anisotropy, as divalent Eu has zero orbital angular momentum. Magnetic interactions are governed by the RKKY interaction (Nakamura et al., 2015). Neutron diffraction has established that the AFM order involves an incommensurate modulation wave (Kaneko et al., 2021). Single-crystal x-ray diffraction (SXRD) has shown the coexistence of the incommensurate CDW modulation and AFM order (Shimomura et al., 2019). Furthermore, Shimomura et al. (2019) proposed a lowering of the lattice symmetry at the third magnetic transition towards $Immm$ orthorhombic. This is essentially different from the present discovery of $Fmmm$ orthorhombic symmetry below the CDW transition.

EuAl$_4$ possesses a 3D band structure with localized $4f$ electrons of Eu well below the Fermi surface (Kobata et al., 2016). The CDW mainly involves orbitals of the Al atoms (Kaneko et al., 2021). This is in agreement with the observation of a CDW with $T_{CDW} = 243$ K in isostructural SrAl$_4$, where non-magnetic Sr replaces Eu (Nakamura et al., 2016; Niki et al., 2020). Here we present electronic band-structure calculations for the tetragonal structure of EuAl$_4$. They confirm that the location of the CDW is on the Al atoms. They reveal a 3D band structure with a highly structured Fermi surface.
2. Experimental and Computational details

Single-crystals of EuAl\(_4\) were synthesized by the Al self-flux method. The elements europium (Lieco, 99.9\% purity) and aluminum (Alfa Aesar, 99.999\%) were filled into an alumina crucible in the ratio 1:20. The crucible was sealed in an evacuated quartz glass ampoule. It was heated to a temperature of 1323 K and held at this temperature for 24 hours. After which the crucible was cooled down to 1073 K in 6 hours and then slowly cooled at a rate of 2 K/hr down to 923 K at which point the crystals were separated from the molten metal by centrifugation. The 1:4 stoichiometry of the product was confirmed by energy-dispersive x-ray spectroscopy (EDX) as well as by the structure refinements against SXRD data.

X-ray diffraction experiments were performed at Beamline P24 of PETRA-III at DESY in Hamburg, employing radiation of a wavelength of 0.5000 Å. The temperature of the specimen was controlled by a CRYOCOOL open-flow helium gas cryostat. Complete data sets of intensities of Bragg reflections were measured at temperatures of 250 K (tetragonal phase), and of 70 K and 20 K (CDW phase). Each run of data collection comprises 3640 frames, corresponding to a rotation of the crystal over 364 deg, which was repeated 10 times. These data were binned to a data set of 364 frames of 1 deg of rotation and 10 seconds exposure time, using the SNBL toolbox (Dyadkin et al., 2016). See Section S1 in the supporting information.

The EVAL15 software suite (Schreurs et al., 2010) has been used for processing the SXRD data. At 250 K a single run was collected at a crystal-to-detector distance of at 110 mm and without a 2\(\theta\) offset of the detector. At 70 K and at 20 K a crystal-to-detector distance of 260 mm required two runs, with and without 2\(\theta\) offset, respectively. The two binned runs for 70 K and those for 20 K were integrated separately, and subsequently merged in the module ANY of EVAL15. SADABS (Sheldrick, 2008) has been used for scaling and absorption correction with Laue symmetry 4/\textit{mmm}
for the 250 K data and \textit{mmm} for 70 K and 20 K. The reflection file produced was imported to Jana2006 (Petricek \textit{et al.}, 2014; Petricek \textit{et al.}, 2016). Table 1 shows the crystallographic information.

The magnetic susceptibility $\chi(T)$ has been measured for temperatures 2.5–300 K, using a commercial SQUID magnetometer (MPMS5 by Quantum Design, USA). Measurements have been made in fields of 0.1 T and 0.5 T.

The specific heat, $C_p(T)$, has been measured from 220 to 8 K by the thermal relaxation method, using a physical property measuring system (PPMS, Quantum Design, USA).

Density functional theory (DFT) based calculations were performed within the generalized gradient approximation (GGA) using the projector augmented (PAW) wave method as implemented in the Vienna \textit{Ab-initio} Simulation Package (VASP) (Kresse & Joubert, 1999; Kresse & Furthmüller, 1996). The Perdew-Burke-Ernzerhof (PBE) functional was used to consider the exchange-correlation effects (Perdew \textit{et al.}, 1996). An energy cutoff of 380 eV was used for the plane-wave basis set, and a $\Gamma$-centered, $9 \times 9 \times 9$ $k$ mesh was employed for the bulk Brillouin zone sampling. Spin-orbit coupling effects were considered in all the calculations. We employed Eu$^{2+}$ by considering the remaining 4$f$ electrons as core electrons. A tight-binding Hamiltonian was generated to compute the Fermi surface on a finer $k$ grid (Marzari & Vanderbilt, 1997). The FermiSurfer software package was used to visualize the Fermi surface (Kawamura, 2019).

3. Discussion

3.1. Analysis of the CDW structure

SXRD at 250 K confirmed the $I4/mmm$ crystal structure of EuAl$_4$. The SXRD data at 70 K revealed satellite reflections at positions that can be described by the modulation wave vector $\mathbf{q} = (0, 0, 0.1781(3))$, in agreement with the results by Naka-
mura et al. (2015) and Shimomura et al. (2019). Visualisation of the SXRD data was done with aid of the software CrysAlisPRO (Rigaku, 2019). Figs. 2(a) and 2(b) show a small part of the \((0, k, l)\) plane of the reconstructed reciprocal lattice. Satellite reflections along \(\mathbf{c}^*\) are clearly visible at 70 K [Fig. 2(b)]. Upon further cooling to 20 K, there is a reduction by 0.004 in the \(\sigma_3\) component of the modulation wave vector, in agreement with Shimomura et al. (2019).

We note that the lattice parameters in the CDW phase do not give evidence for an orthorhombic lattice distortion. This could explain why earlier works have not found this symmetry lowering.

In order to determine the crystal structure of the CDW phase, we have tested different superspace groups for its symmetry (See Table S2 in the supporting information). It is noticed that the tetragonal lattice allows two fundamentally different orthorhombic lattices as subgroups: \(I\text{mmm}\) preserves the mirror planes perpendicular to the \(a\) and \(b\) axes of \(I\text{4/mmm}\), while \(F\text{mmm}\) preserves the diagonal mirror planes. Table 2 provides the crystallographic data for three of the refined crystal structures (compare Table S2 in the supporting information). The three models, A, B and C, are discussed below.

3.1.1. Model A: In the diffraction pattern we did not observe any splitting of the main or satellite reflections, where split reflections would indicate a twinned crystal of lower symmetry. Also, we did not find a distortion in the lattice parameters, as it would occur for a single-domain crystal of lower symmetry. Furthermore, the preservation of tetragonal symmetry within the CDW phase was reported in the literature (Nakamura et al., 2015; Shimomura et al., 2019). Therefore, initial data processing was performed under the assumption of tetragonal symmetry, employing point group \(4/m\text{mmm}\) for scaling and absorption correction in SADABS (Sheldrick, 2008)).
ture refinements of the incommensurately modulated structure were performed with a model with superspace group $I4/mmm(00\sigma)0000$. Table 2 shows that $R_{int}$ as well as $R_F$ for the main reflections are reasonably low, indicating that the average structure of the CDW phase still is tetragonal in good approximation. This conclusion is reinforced by the fact that refinement of the average structure against main reflections leads to $R_F = 1.55\%$; an excellent fit. However, $R_F = 60.46\%$ for the satellite reflections. This high value indicates that the satellite reflections are not well fitted and that the CDW modulation does not have tetragonal symmetry.

This makes Model A an unsuitable candidate for the incommensurate CDW structure. Other tetragonal superspace groups were also tested, leading to similar failures in describing the modulation wave or with reflection conditions violated by the measured SXRD data (see Table S2 in the supporting information). As a result we can rule out tetragonal symmetry for the modulated CDW crystal structure.

3.1.2. Model B: As second model we have considered a lowering of the symmetry from tetragonal $I4/mmm$ to its orthorhombic subgroup $Immm$. This orthorhombic point symmetry was used for scaling and absorption correction of the SXRD data in SADABS (Sheldrick, 2008)). The CDW phase transition allows for pseudomerohedral twinning of two, differently oriented domains on the tetragonal lattice, that are related by the missing fourfold rotation (Parsons, 2003). Since split reflections or a lattice distortion could not be detected in the SXRD data, all Bragg reflections have contributions from both domains. The structure refinement of a model in superspace group $Immm(00\sigma)s00$ has lead to a twin volume ratio of 0.485 : 0.515, thus explaining the nearly tetragonal point symmetry of the SXRD data. $R$-values indicate a good fit to the SXRD data for this model (Table 2). As a result, this model is a prime candidate for describing the incommensurately modulated crystal structure of the CDW.
phase.

3.1.3. Model C: As last model we present model C with symmetry according to \( Fm\overline{mmm} \), the other orthorhombic subgroup, which now preserves the diagonal mirror planes of \( I\overline{4}/mmm \). Scaling and absorption correction of the SXRD data was performed with SADABS according to the differently oriented point group \( mmm \) (Sheldrick, 2008). Again, two domains are possible that are related by the missing four-fold rotation. The structure refinement of a model in superspace group \( Fm\overline{mmm}(00\sigma)s00 \) has lead to a twin volume ratio of \( 0.454(4) : 0.546 \), thus explaining the nearly tetragonal point symmetry of the SXRD data. \( R \)-values indicate an excellent fit to the SXRD data for this model (Table 2), which is significantly better than that of model B. Furthermore, the refined parameters possess slightly smaller s.u.’s in model C than in model B, while the number of parameters is one smaller in model C (Tables S3 and S4 in the supporting information). Therefore, the best fit to the SXRD data has been obtained for a modulated crystal structure with symmetry according to the superspace group \( Fm\overline{mmm}(00\sigma)s00 \). \( Fm\overline{mmm}(00\sigma)0s0 \) is an alternate setting of this superspace group, while all other symmetries lead to a worse fit to the SXRD data (Table S2 in the supporting information).

Recently, Kaneko et al. (2021) have proposed that the CDW of EuAl\(_4\) involves displacements of the Al atoms perpendicular to \( c \), while Eu would not be involved in the PLD. The present crystal structure involves atomic modulations exclusively perpendicular to \( c \), as it is enforced by the superspace symmetry (Table S4). However, the modulation amplitudes are of comparable magnitude for all three atoms, Eu, Al1 and Al2. Nevertheless, a non-zero modulation amplitude is not evidence by itself, that the involved atom must contribute electronic states to the CDW. The atomic modulation may also be caused by the elastic coupling to other atoms that are carrying
the CDW. In EuAl$_4$, the shortest interatomic distances are between Al2 atoms and for Al1–Al2 [Fig. 3(a)]. They are hardly modulated, and forming a two-dimensional network of Al perpendicular to c (Fig. 1). The largest modulation is found for the next shorter Al–Al distance between Al1 atoms [Fig. 3(b)]. This strong modulation suggests that the CDW resides on the layers of Al atoms. Eu is elastically coupled to Al1 and Al2 (Fig. S1) and is not part of the CDW. The $t$ plots of interatomic distances cannot elaborate on the precise location: the CDW resides either on the Al1 atoms or on a network of Al1 and Al2 atoms (Fig. 3).

### 3.2. Electronic structure and Fermi surface

Figure 4(a) shows the calculated band structure along the high-symmetry directions in the primitive Brillouin zone of the periodic crystal structure of EuAl$_4$ with $I4/mmm$ symmetry. Both the valence and conduction bands cross the Fermi level $E_F$, resolving its metallic ground state. Importantly, the bands along $\Gamma$–$Z$ have a substantial energy dispersion. This indicates the three-dimensional nature of the Fermi surface as discussed below. There is a Dirac nodal crossing above the Fermi level along the $\Gamma$–$Z$ direction, which is protected by $C_{4z}$ rotational symmetry. EuAl$_4$ thus realizes a Dirac semimetallic state. To resolve the electronic states near $E_F$, we present the atom-projected density of states (PDOS) in Fig. 4(b); Eu PDOS is in blue and Al PDOS is in red. The Al states are dominant at $E_F$, indicating that Al atoms are predominantly metallic and more likely undergo CDW modulations, in agreement with the analysis of PLD (Section 3.1) and the literature. PDOS of Eu comprises of $d$ states at the Fermi level, while $4f$ states are well below $E_F$, in agreement with the literature (Kobata et al., 2016).

We present the calculated Fermi pockets associated with the valence ($h^+$) and conduction states ($e^-$) in Figs. 4(c,d). They reveal a hole pocket centered on $\Gamma$ and an
electron Fermi pocket centered on $Z$. Both Fermi pockets are highly structured. The $e^-$ Fermi pocket suggest the possibility of nesting perpendicular to the $c$ axes. For the $h^+$ pocket a possible FSN is not clearly resolved. It should however be noted that because of the 3D nature of the Fermi surface, the nesting may have a complicated structure. These results do not clearly indicate FSN as mechanism for the formation of the CDW state in EuAl$_4$.

3.3. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility, measured with magnetic fields of 0.1 T and 0.5 T, is shown for 2.4–300 K in Fig. 5. Any change of the susceptibility at the CDW transition (e.g. as a change of Pauli paramagnetism) is masked by the large value of the paramagnetic susceptibility. However, the low temperature data reveal an AFM transition below 16 K, which agrees with the previously published value (Nakamura et al., 2015).

3.4. Specific heat

The temperature dependence of the specific heat ($C_p$) is shown for 8–210 K in Fig. 6. The high temperature data clearly reveal a small, broad jump of $\Delta C_p = 2.5$ J/(mol K) at 145 K, suggesting a thermodynamic phase transition (CDW) at 145 K. Such an anomaly in the temperature dependence of the specific heat is consistent with that observed in canonical CDW systems, like NbSe$_3$ (Tomić et al., 1981). The low-temperature data display multiple AFM transitions, which have also been observed in earlier studies (Nakamura et al., 2015).
4. Conclusions

EuAl$_4$ possesses the BaAl$_4$ crystal structure type with tetragonal symmetry $I4/mmm$. It undergoes a CDW transition at $T_{CDW} = 145$ K. Here, we have presented the incommensurately modulated crystal structure of EuAl$_4$ in its CDW state. Structure refinements according to the superspace approach have shown that: (i) the modulation is incommensurate with modulation wave vector $\mathbf{q} = (0,0,0.1781(3))$ at 70 K, in agreement with Shimomura et al. (2019); and (ii) the symmetry of the CDW crystal structure is orthorhombic with superspace group $Fmmm(00\sigma)s00$, where $Fmmm$ is a subgroup of $I4/mmm$ of index 2. Despite this group–subgroup relation, we did not find any lattice distortion in the SXRD data. Even more, atomic positions of the basic structure of $Fmmm(00\sigma)s00$ still obey the $I4/mmm$ symmetry (Table S3). Symmetry breaking is entirely in the modulation wave (CDW and PLD), where atoms Eu and Al1 have displacements exclusively along a of the $F$-centered unit cell (Table S4), while the fourfold rotation would require equal displacement amplitudes along a and b.

One interesting question is the location of the CDW. Analysis of the modulation of interatomic distances (Section 3.1) as well as features of the electronic band structure (Section 3.2) have indicated the Al atoms as supporting the CDW, in agreement with the literature (Kobata et al., 2016; Kaneko et al., 2021).

Compounds of rare earth ($R$) and transition metals, like $R_5\text{Ir}_4\text{Si}_{10}$ and $R_2\text{Ir}_3\text{Si}_5$, contain highly correlated electron systems, with accompanying influence on the mechanism of formation of CDWs. In EuAl$_4$, the majority element is the light $p$-block metal aluminum. Band-structure calculations have shown that FSN is a possible mechanism of CDW formation. Furthermore, the weak anomaly in $C_p(T)$ near $T_{CDW}$ is similar to anomalies of canonical CDW materials and it is much smaller than observed for the rare-earth–transition-metal base compounds, again this would support the FSN mech-
anism. An alternative possibility is that the CDW is related to nesting of nontrivial bands that are present in the band structure (Shi et al., 2021; Chiu et al., 2022).

The present discovery of orthorhombic symmetry for the CDW state of EuAl$_4$ is important for modeling of the electronic properties of the CDW state as well as for identifying the correct magnetic order and understanding the magnetic properties of the four AFM states below 16 K.

Recent work either has used tetragonal symmetry for analysing the AFM states (Shang et al., 2021; Kaneko et al., 2021). Alternatively, Shimomura et al. (2019) have proposed orthorhombic $Immm$ symmetry for the third AFM state. This orthorhombic subgroup incorporates the perpendicular mirror planes of $I4/mmm$, while presently found $Fmmm$ is based on the diagonal mirror planes of $I4/mmm$. On the other hand, Shimomura et al. (2019) report peak splitting in neutron diffraction into "three maxima." Together with the present observation of lowering of symmetry at the CDW transition, this suggests that the third AFM state could have monoclinic symmetry ($c$ unique) instead of orthorhombic symmetry, since, apparently, both the diagonal and perpendicular mirror planes are lost.

Acknowledgements We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III, using beamline P24. Beamtime was allocated for proposal I-20190810. J.-K. Bao acknowledges the Alexander von Humboldt Foundation for financial support.

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| Temperature (K) | 250  | 70   | 20   |
|----------------|------|------|------|
| Crystal system | Tetragonal | Orthorhombic | Orthorhombic |
| Space group; SSG | I4/mmm | Fmmm(00σ)s00 | Fmmm(00σ)s00 |
| No. | 139 | 69.1.17.2 | 69.1.17.2 |
| a (Å) | 4.3949(1) | 6.1992(4) | 6.1991(3) |
| b (Å) | 4.3949 | 6.2001(4) | 6.1987(4) |
| c (Å) | 11.1607(3) | 11.1477(3) | 11.1488(4) |
| Volume (Å³) | 215.57(1) | 428.47(4) | 428.41(4) |
| Wavevector, qz | - | 0.1781(3) | 0.1741(2) |
| Z | 2 | 4 | 4 |
| Wavelength (Å) | 0.50000 | 0.50000 | 0.50000 |
| Detector distance (mm) | 110 | 260 | 260 |
| 2θ-offset (deg) | 0 | 0, 25 | 0, 25 |
| χ-offset (deg) | -60 | -60 | -60 |
| Rotation per image (deg) | 1 | 1 | 1 |
| (sin(θ)/λ)max (Å⁻¹) | 0.682610 | 0.748910 | 0.749031 |
| Absorption, µ (mm⁻¹) | 5.8373 | 5.9090 | 5.9100 |
| Tmin, Tmax | 0.3211, 0.3712 | 0.3209, 0.3732 | 0.3192, 0.3676 |
| Criterion of observability | I > 3σ(I) | I > 3σ(I) | I > 3σ(I) |
| Number of main reflections | | | |
| measured | 1407 | 473 | 470 |
| unique (obs/all) | 109/109 | 174/174 | 176/176 |
| Number of satellites | | | |
| measured | - | 929 | 928 |
| unique (obs/all) | - | 279/316 | 263/322 |
| Rint main (obs/all) | 0.0374/0.0374 | 0.0136/0.0136 | 0.0188/0.0188 |
| Rint sat (obs/all) | - | 0.0581/0.0588 | 0.0606/0.0616 |
| No. of parameters | 9 | 18 | 18 |
| RF main (obs) | 0.0147 | 0.0165 | 0.0213 |
| RF sat (obs) | - | 0.0369 | 0.0311 |
| wRF main (all) | 0.0214 | 0.0203 | 0.0230 |
| wRF sat (all) | - | 0.0395 | 0.0336 |
| wRF all (all) | 0.0214 | 0.0245 | 0.0250 |
| GoF (obs/all) | 1.53/1.53 | 1.13/1.09 | 0.93/0.88 |
| Δρmin, Δρmax (e Å⁻³) | -1.35, 1.15 | -2.40, 3.58 | -1.49, 1.58 |
Table 2. Crystallographic data for three models for the modulated crystal structure at 70 K, based on different superspace groups. Criterion of observability: $I > 3\sigma(I)$

| Model | A          | B          | C          |
|-------|------------|------------|------------|
| $a$ (Å) | 4.3834(3) | 4.3835(3) | 6.1992(4) |
| $b$ (Å) | 4.3834   | 4.3841(3) | 6.2001(4) |
| $c$ (Å) | 11.1488(4)| 11.1475(3)| 11.1477(3)|
| $V$ (Å³) | 214.21(2)| 214.23(2) | 428.47(4) |
| $q$    | 0.1782(3)c* | 0.1781(3)c* | 0.1781(3)c* |
| SSG    | $I4/mmm(000)000$ | $I4/mmm(000)000$ | $I4/mmm(000)000$ |
| $R_{int}$ main (obs/all)% | 1.53/1.53 | 1.28/1.28 | 1.36/1.36 |
| $R_{int}$ sat (obs/all)% | 7.43/7.49 | 6.75/6.85 | 5.81/5.88 |
| $R_F$ main (obs/all)% | 4.37/4.37 | 1.96/1.96 | 1.65/1.65 |
| $R_F$ sat (obs/all)% | 60.46/70.53 | 5.25/5.83 | 3.69/4.05 |
| Unique main (obs/all) | 130/130 | 225/225 | 174/174 |
| Unique sat (obs/all) | 215/254 | 365/425 | 279/316 |
| No. of parameters | 13 | 19 | 18 |

Fig. 1. Crystal structure of EuAl$_4$ with space group $I4/mmm$ in the periodic phase at 250K. Depicted is the $I$-centered unit cell with basis vectors $a_I$, $b_I$ and $c_I$. Brown spheres correspond to the Eu atoms; dark blue spheres represent Al1 atoms; and green spheres stand for Al2 atoms. Shortest interatomic distances are: $d[\text{Eu–Eu}] = 4.3949(2)$ Å, $d[\text{Al1–Al1}] = 3.1077(1)$ Å, $d[\text{Al2–Al1}] = 2.664(1)$ Å and $d[\text{Al2–Al2}] = 2.568(4)$ Å.
Fig. 2. Excerpt of the reconstructed reciprocal layer \((0kI)\) for SXRD data measured at (a) \(T = 250\) K, and (b) 70 K. Indices are given for several main reflections. Panel (b) is better resolved than panel (a), because of the longer crystal-to-detector distance at 70 K. Dark bands are due to insensitive pixels between the active modules of the PILATUS3 X CdTe 1M detector.

Fig. 3. \(t\)-Plot of interatomic distances (Å) \(d[Al1–Al1]\), \(d[Al2–Al1]\) and \(d[Al2–Al2]\) at 70 K, where the first atom is the central atom. The number on each curve is the number of the symmetry operator that is applied to the second atom of the bond pair. Symmetry operators are listed in Table S5 in the supporting information.
Fig. 4. (a) Bulk band structure and (b) Density-of-states (DOS) of EuAl$_4$. The dashed lines in (a) and (b) mark the Fermi level at energy ($E$) zero. The calculated (c) hole (blue) and (d) electron (yellow) Fermi pockets in the primitive bulk Brillouin zone. Three-dimensionally (3D) structured hole and electron Fermi pockets are resolved.
Fig. 5. Temperature dependent magnetic susceptibility of EuAl$_4$ from 2.4 to 300 K. Data measured in fields of 0.1 T and 0.5 T.

Fig. 6. Temperature dependence of the specific heat $C_p$ from 8 to 210 K. The lower inset (a) provides an enlarged view around the anomaly at 145 K, where $\Delta C = 2.5$ J/(mol K). The upper inset (b) displays $C_p$ vs $T$ at low temperatures 8–25 K.

Synopsis

The incommensurate charge-density-wave of EuAl$_4$ below $T_{CDW} = 145$ K is found to possess orthorhombic symmetry, despite an average crystal structure that remains tetragonal in very good approximation. This finding has ramifications for the interpretation of all physical properties of EuAl$_4$, in particular its multiple magnetic transitions.