Coupling between colossal charge density wave ordering and magnetism in Ho$_2$Ir$_3$Si$_5$

Sitaram Ramakrishnan,*,† Jin-Ke Bao,‡,¶ Claudio Eisele,‡ Bikash Patra,§ Minoru Nohara,† Biplab Bag,§,∥ Leila Noohinejad,¶ Martin Tolkiehn,⊥ Carsten Paulmann,⊥,# Achim M. Schaller,‡ Toms Rekis,‡ Surya Rohith Kotla,‡ Andreas Schönleber,‡ Arumugam Thamizhavel,§ Bahadur Singh,*,§ Srinivasan Ramakrishnan,*,§,@ and Sander van Smaalen*,‡

†Department of Quantum Matter, AdSE, Hiroshima University, Higashi-Hiroshima 739-8530, Japan
‡Laboratory of Crystallography, University of Bayreuth, 95447 Bayreuth, Germany
¶Department of Physics, Materials Genome Institute and International Center for Quantum and Molecular Structures, Shanghai University, Shanghai 200444, People’s Republic of China
§Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400005, India
∥Amity Institute of Applied Sciences, Amity University Jharkhand, India-834001
⊥P24, PETRA III, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany
#Mineralogisch-Petrographisches Institut, Universität Hamburg, 20146 Hamburg, Germany
@IISER, Dr. Homi Bhabha Road, Pashan, Pune-411008, India

E-mail: niranj002@gmail.com; bahadur.singh@tifr.res.in; ramky07@gmail.com; smash@uni-bayreuth.de

Abstract
$\text{Ho}_2\text{Ir}_3\text{Si}_5$ belongs to the family of three-dimensional (3D) $R_2\text{Ir}_3\text{Si}_5$ ($R =$ Lu, Er and Ho) compounds that exhibit a colossal first-order charge density wave (CDW) transition where there is a strong orthorhombic-to-triclinic distortion of the lattice accompanied by superlattice reflections. The analysis by single-crystal X-ray diffraction (SXRD) has revealed that the Ir-Ir zigzag chains along $c$ are responsible for the CDW in all three compounds. The replacement of the rare earth element from non-magnetic Lu to magnetic Er or Ho lowers $T_{\text{CDW}}$, where $T_{\text{CDW, Lu}} = 200$ K, $T_{\text{CDW, Er}} = 150$ K and $T_{\text{CDW, Ho}} = 90$ K. Out of the three compounds, $\text{Ho}_2\text{Ir}_3\text{Si}_5$ is the only system where second-order superlattice reflections could be observed, indicative of an anharmonic shape of the modulation wave. The CDW transition is observed as anomalies in the temperature dependencies of the specific heat, electrical conductivity and magnetic susceptibility, which includes a large hysteresis of 90 to 130 K for all measured properties, thus corroborating the SXRD measurements. Similar to previously reported $\text{Er}_2\text{Ir}_3\text{Si}_5$, there appears to be a coupling between CDW and magnetism such that the $\text{Ho}^{3+}$ magnetic moments are influenced by the CDW transition, even in the paramagnetic state. Moreover, earlier investigations on polycrystalline material revealed antiferromagnetic (AFM) ordering at $T_N = 5.1$ K, whereas AFM order is suppressed and only the CDW is present in our highly ordered single-crystal. First-principles calculations predict $\text{Ho}_2\text{Ir}_3\text{Si}_5$ to be a metal with coexisting electron and hole pockets at the Fermi level. The Ho and Ir atoms have spherically symmetric metallic-type charge density distributions that are prone to CDW distortion. Phonon calculations affirm that the Ir atoms are primarily responsible for the CDW distortion, which is in agreement with the experiment.
Introduction

Structural phase transitions, such as the development of charge density waves (CDWs), have attracted continued interest from condensed-matter physicists and chemists. Originally, the manifestation of a CDW was proposed to originate in Fermi surface nesting (FSN), as it is present in quasi-one-dimensional metals (1D). More recently, alternative mechanisms were proposed that explain, for example, the formation of CDWs by \( q \)-dependent electron-phonon coupling (EPC) in three-dimensional (3D) CDW compounds. Examples of 3D metals with CDWs include \( \alpha \)-Uranium, \( \text{CuV}_2\text{S}_4 \), \( \text{La}_3\text{Co}_4\text{Sn}_{13} \), \( \text{RTe}_3 \) \( (R = \text{La, Sm, Gd, Tb, Dy, Ho, Er, Tm}) \), \( \text{RTe}_2 \) \( (R = \text{La, Ce}) \), \( \text{R}_5\text{Ir}_4\text{Si}_{10} \) \( (R = \text{Dy, Ho, Er, Yb, Lu}) \), \( \text{Sm}_2\text{Ru}_3\text{Ge}_5 \), \( \text{EuAl}_4 \), and \( \text{CuIr}_2-x\text{Cr}_x\text{Te}_4 \). In several of these compounds a coexistence and competition exists between the CDW and antiferromagnetic (AFM) order or superconductivity (SC).

In the family of compounds \( \text{R}_3\text{NiC}_2 \) \( (R = \text{Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm}) \), the CDW competes with AFM. In the case of \( \text{SmNiC}_2 \) ferromagnetic (FM) order completely destroys the CDW. On the other hand, Kolincio et al. have established the coexistence of a CDW and field-induced FM order in \( \text{TmNiC}_2 \), suggesting strong coupling of the rare-earth spins to the CDW in these rare-earth materials. However, the magnetic susceptibility of the paramagnetic regime does not exhibit anomalies at the CDW transitions.

\( \text{Er}_2\text{Ir}_3\text{Si}_5 \) differs from most magnetic CDW compounds, in that the magnetic susceptibility of the paramagnetic state exhibits an anomaly at the CDW transition. Presently, we report a similar effect for \( \text{Ho}_2\text{Ir}_3\text{Si}_5 \). On the other hand, the CDW of non-magnetic \( \text{Lu}_2\text{Ir}_3\text{Si}_5 \) coexists with SC at low temperatures.

Investigations of the CDW in \( \text{Lu}_2\text{Ir}_3\text{Si}_5 \) has been extensively done. Studies by transmission electron microscopy (TEM) reported the modulation wave vector as \( \mathbf{q} = \sigma(\overline{121}) \) with \( \sigma = 0.23-0.25 \) around 200 K. Recently, the modulated crystal structure of \( \text{Lu}_2\text{Ir}_3\text{Si}_5 \) was reported as similar to that of \( \text{Er}_2\text{Ir}_3\text{Si}_5 \). In both systems it was elucidated that the CDW resides on the zigzag chains of Ir atoms along \( \mathbf{c} \). Although the rare earth element is not directly involved in the stabilization of the CDW, we have earlier proposed that it would
indirectly influence the CDW through its size (atomic radius). Er has a larger atomic radius than to Lu has (2.26 vs 2.17 Å), while the transition occurs 50 K lower in Er$_2$Ir$_3$Si$_5$ than in Lu$_2$Ir$_3$Si$_5$. Here, we find that there is no such simple relationship between atomic radius and $T_{CDW}$. The atomic radii of Ho and Er are equal, but $T_{CDW} = 90$ K of Ho$_2$Ir$_3$Si$_5$ is much lower than $T_{CDW} = 150$ K of Er$_2$Ir$_3$Si$_5$.

From SXRD we found that Ho$_2$Ir$_3$Si$_5$ undergoes a large distortion of the lattice where the symmetry is lowered from orthorhombic ($Ibam$) to triclinic ($I\bar{1}$) below the transition temperature $T_{CDW}$. Simultaneously, superlattice reflections appear at incommensurate positions, with values of $q = [0.2494(2), 0.4978(2), 0.2488(2)]$ at 70 K. The CDW is supported by zigzag chains of Ir atoms in all three compounds $R_2$Ir$_3$Si$_5$. Ho$_2$Ir$_3$Si$_5$ differs from Lu$_2$Ir$_3$Si$_5$ and Er$_2$Ir$_3$Si$_5$ by the presence of second-order superlattice reflections in its SXRD, indicative of anharmonic contributions to the displacive modulation wave.

We present for Ho$_2$Ir$_3$Si$_5$ the temperature dependencies of the electrical resistivity $\rho(T)$, the specific heat $C_p(T)$ and the magnetic susceptibility $\chi(T)$. They show anomalies in agreement with a first-order CDW transition with a hysteresis of about 40 K. Due to the strain imposed by the transition onto the crystal, it cracks which can be seen clearly from the resistivity measurements. Such cracking of crystals has also been observed in other CDW compounds, like BaFe$_2$Al$_9$. From the magnetic susceptibility we observed that there is an influence of the CDW on the effective magnetic moment of Ho$^{3+}$, which is similar to what was reported in Er$_2$Ir$_3$Si$_5$. Such an effect of the CDW on the rare earth spin in the paramagnetic state is not commonly seen in rare earth compounds. Earlier studies have shown that the disorder in the polycrystalline material allows long-range AFM order to develop at low temperatures. However, in the present high-quality single crystal, long-range AFM order is absent and only the CDW is observed. Here, we elucidate the differences and similarities in the incommensurate structure of Ho$_2$Ir$_3$Si$_5$ by comparing with Lu$_2$Ir$_3$Si$_5$ and Er$_2$Ir$_3$Si$_5$. Furthermore, we explore the coupling of the CDW and magnetism of Ho$^{3+}$ spins and absence of long-range AFM order.
Experimental and computational details

Crystal growth and characterization

A single crystal of Ho$_2$Ir$_3$Si$_5$ has been grown by the Czochralski method in a tetra-arc furnace as shown in Fig. 1. We have chosen the Czochralski over flux growth or any other technique because the individual elements have high melting points. Furthermore, iridium metal does not dissolve in most of the typical fluxes. To start with, high purity individual elements of Ho : Ir : Si (99.99% for Ho and Ir, and 99.999% for Si) were taken in the stoichiometric ratio 2 : 3 : 5, amounting to about 8 to 9 g, and melted repeatedly to ensure its homogeneity. Next, a seed crystal was cut from this polycrystalline ingot for the purpose of crystal growth. The polycrystalline seed was gently inserted into the molten solution and initially pulled at a rapid speed of about 80 mm/h. The temperature of the
melt was adjusted such that a necking is formed and then we employed a pulling speed of about 10 mm/h throughout the growth process. About 50 mm long ingot was pulled. Energy-dispersive X-ray spectroscopy (EDX) was used to verify the chemical composition.

**Single-crystal X-ray diffraction (SXRD): data collection and data processing.**

Small pieces of single-crystalline Ho$_2$Ir$_3$Si$_5$ were obtained by crushing a large single crystal, from which crystal A of dimensions 0.15×0.07×0.1 mm$^3$ was selected for a single-crystal X-ray diffraction (SXRD) experiment at beamline P24 of PETRA-III Extension at DESY in Hamburg, Germany. SXRD was measured at station EH2 of beamline P24, employing radiation of a wavelength of $\lambda_{P24} = 0.50000$ Å. For further details regarding data collection refer to the supporting information.

The EVAL15 software suite was used for processing the SXRD data. SADABS was used for scaling and absorption correction, with Laue symmetry mmmm for the data in the periodic phase and $\bar{1}$ for the CDW phase. As the crystal structure in the CDW phase is incommensurately modulated we had to use the superspace approach to index and integrate the data. Section S2 in the supporting information provides further details. The resulting reflection file was imported into JANA2006. Table I gives the crystallographic information at 200 K (periodic phase) and at 70 K (incommensurate phase). The crystallographic data at other temperatures and details regarding SXRD data processing are given in the Supporting Information.

**Physical properties**

A commercial superconducting quantum interference device (SQUID) magnetometer (MPMS5, Quantum Design, USA) was used to measure dc magnetic susceptibility in a field of 100 mT as a function of temperature from 2 to 300 K. The electrical resistivity between 1.8 and 300
Table 1: Crystallographic data of crystal A of Ho$_2$Ir$_3$Si$_5$ at 200 K (periodic phase) and 70 K (CDW phase).

| Temperature (K) | 200 | 70 |
|----------------|-----|----|
| Crystal system | Orthorhombic | Triclinic |
| Space/Superspace group | Ibam | I(σ1 σ2 σ3)0 |
| Space/Superspace group No. | 72 | 2.1.1.1 |
| a (Å) | 9.9023(4) | 9.8356(5) |
| b (Å) | 11.3747(3) | 11.4902(4) |
| c (Å) | 5.7745(3) | 5.7304(3) |
| α (deg) | 90 | 89.983(3) |
| β (deg) | 90 | 91.772(2) |
| γ (deg) | 90 | 89.975(1) |
| Volume (Å$^3$) | 650.42(5) | 647.32(5) |
| Wave vector q | - | (0.2494(2), 0.4978(2), 0.2488(2)) |
| Z | 4 | 4 |
| Wavelength (Å) | 0.50000 | 0.50000 |
| Detector distance (mm) | 110 | 110 |
| 2θ-offset (deg) | 0 | 0 |
| χ-offset (deg) | -60 | -60 |
| Rotation per image (deg) | 1 | 1 |
| (sin(θ)/λ)$_{\text{max}}$ (Å$^{-1}$) | 0.683589 | 0.684039 |
| Absorption, μ (mm$^{-1}$) | 34.823 | 34.990 |
| T$_{\text{min}}$, T$_{\text{max}}$ | 0.0220, 0.0501 | 0.0230, 0.0501 |
| Criterion of observability | $I > 1.5σ(I)$ | $I > 1.5σ(I)$ |
| Number of ($m = 0$) reflections | | |
| measured | 3765 | 2706 |
| unique (obs/all) | 451/470 | 1298/1474 |
| Number of ($m = 1$) reflections | | |
| measured | - | 12770 |
| unique (obs/all) | - | 2779/6454 |
| Number of ($m = 2$) reflections | | |
| measured | - | 12725 |
| unique (obs/all) | - | 714/3263 |
| $R_{\text{int}}$ ($m = 0$) (obs/all) | 0.0487/0.0487 | 0.0287/0.0288 |
| $R_{\text{int}}$ ($m = 1$) (obs/all) | - | 0.0828/0.1051 |
| $R_{\text{int}}$ ($m = 2$) (obs/all) | - | 0.0967/0.1833 |
| No. of parameters | 31 | 147 |
| $R_F$ ($m = 0$) (obs) | 0.0296 | 0.0578 |
| $R_F$ ($m = 1$) (obs) | - | 0.0798 |
| $R_F$ ($m = 2$) (obs) | - | 0.2148 |
| w$R_F$ ($m = 0$) (all) | 0.0380 | 0.0717 |
| w$R_F$ ($m = 1$) (all) | - | 0.0973 |
| w$R_F$ ($m = 2$) (all) | - | 0.3748 |
| w$R_F$ all (all) | 0.0380 | 0.0879 |
| GoF (obs/all) | 1.83/1.33 | 1.69/1.23 |
| $\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e Å$^{-3}$) | -3.00, 2.94 | -14.56, 14.53 |
K was measured by the standard dc four probe technique on a commercial physical property measurement system (PPMS, Quantum Design, USA). The specific heat data were measured both on PPMS as well as using a commercial differential scanning calorimeter (DSC) setup.

**Density functional theory calculations**

Density functional theory (DFT) based calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP). Exchange-correlation effects were included using the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation. A $8 \times 10 \times 12$ $\Gamma$-centered $k$-mesh was used for the Brillouin zone (BZ) sampling with an energy cut-off of 380 eV for the plane-wave basis set. Spin-orbit coupling (SOC) effects were taken into account self-consistently to consider the relativistic effects. We employed Ho$^{3+}$ potential by considering the remaining $4f$ electrons as core electrons. Experimental lattice parameters were used, while the internal atomic positions were relaxed until the residual forces on each atom were less than 0.0001 eV/Å. The VESTA program was used to visualize the charge density distributions. The phonon spectrum was obtained using a $2 \times 2 \times 2$ supercell following the frozen phonon method as implemented in the phonopy package.

**Results and discussion**

**Analysis of the CDW structure**

Unlike Er$_2$Ir$_3$Si$_5$, the manifestation of the CDW appears to be sluggish in Ho$_2$Ir$_3$Si$_5$. The crystal was initially cooled from room temperature down to 70 K, where it remained in the orthorhombic phase, despite $T_{CDW}$ being about 90 K according to the physical property measurements.

It is possible that the crystal was cooled too rapidly, thereby not allowing it to settle in the CDW phase, and resulting in an undercooled state. Upon further lowering of the tem-
perature to 20 K, we observed the coexistence of orthorhombic and CDW phases, indicative of a first-order transition (Figs. 2 and 3). The CDW phase is characterized by superlattice reflections at positions $\mathbf{q} = [0.2496(3), 0.4987(3), 0.2493(3)]$, accompanied by a large monoclinic distortion of the lattice ($\beta = 91.784(3)$ deg), similar to $R_2\text{Ir}_3\text{Si}_5$ ($R = \text{Lu, Er}$) (details are given in the Supporting Information\textsuperscript{40}).

The severity of the distortions induces a colossal strain in the crystal, causing the diffraction spots in SXRD to become broad and elongated [Figs. 2(b) and 2(c)], resulting in many partially overlapped reflections which cannot be used for structural analysis. Sometimes the strain is too much for the crystal to handle, such that it physically shatters, rendering it unusable for further investigations. Such destructive behaviour of the CDW has also been reported for BaFe$_2$Al$_9$.\textsuperscript{38}

Another important difference to Lu$_2\text{Ir}_3\text{Si}_5$ and Er$_2\text{Ir}_3\text{Si}_5$ is that we observe in SXRD on Ho$_2\text{Ir}_3\text{Si}_5$ second-order superlattice reflections ($m = 2$) in addition to first-order superlattice reflections ($m = 1$) [Figs. 2(e) and 2(f)]. The orthorhombic phase disappears after the crystal is heated to 50 K, and only the CDW phase remains at temperatures 50–130 K (Figs. 2(c) and 3). Further heating to 150 and 200 K causes the crystal to enter the orthorhombic phase and the CDW phase disappears [Fig. 2(a)]. Similar to Lu$_2\text{Ir}_3\text{Si}_5$ and Er$_2\text{Ir}_3\text{Si}_5$, there is a lowering of the point symmetry from orthorhombic to triclinic which causes the crystal to be twinned with four orientations.\textsuperscript{52}

Figure 3 shows the temperature dependence of the lattice parameters. One can observe the clear distortion of the lattice upon entering the CDW state, including an expansion of $b$ and contractions of $a$ and $c$. Furthermore, the change in lattice type at $T_{\text{CDW}}$ appears discontinuous, in agreement with the first-order character of the phase transition. Barring 20 K and 130 K as 20 K is an undercooled mixed state and 130 K is on the onset of $T_{\text{CDW}}$ warming and therefore unreliable, it can be inferred from Fig. 3(d) that the modulation wave vector $\mathbf{q}$ decreases with temperature.

The presence of second-order satellite reflections required refinement of the crystal struc-
Figure 2: (a), (b), (c) The \( h0l \) plane, and (d), (e), (f) the \( hkh \) plane reconstructed from measured SXRD data. (a), (d) are for SXRD on the periodic phase at 200 K. (b), (e) show the intermediate phase (undercooled state), where threefold splitting of the reflections can be observed at 20 K, indicating coexistence of CDW and periodic phases. (c), (f) are for SXRD on the CDW phase at 50 K, showing groups of two instead of groups of three split reflections. The degree of splitting increases with the value of \( h \). Panels (e) and (f) show satellite reflections of order \( m = 2 \).
Figure 3: Temperature dependence of (a) the lattice parameters $a$, $b$ and $c$ relative to their values at $T = 200$ K: $a(200) = 9.9023(4)$, $b(200) = 11.3747(3)$ and $c(200) = 5.7745(3)$ Å; (b) the lattice parameters $\alpha$, $\beta$ and $\gamma$; (c) the volume of the unit cell; and (d) components of the modulation wave vector $\mathbf{q}$. Orange and blue symbols refer to data obtained during heating and cooling of the crystal, respectively. The undercooled state at 20 K has coexisting CDW and periodic phases.
ture with higher order harmonics for the modulation functions. Table 2 provides a comparison of the models to see which provides the best fit to the SXRD data in the CDW phase.

Table 2: Quality of the fit to the SXRD data at 70 K for three structure models for the CDW phase. See text for models A, B and C. The number of unique reflections is 1298/1474 for obs/all main reflections \((m = 0)\), 2779/6454 for obs/all \(m = 1\) satellites, and 714/3263 for obs/all \(m = 2\) satellites. Criterion of observability is \(I > 1.5\sigma(I)\).

| Models          | A   | B   | C   |
|-----------------|-----|-----|-----|
| No. of parameters | 147 | 177 | 177 |
| \(R_F\) \((m = 0)\) (obs) | 0.0578 | 0.0577 | 0.0535 |
| \(R_F\) \((m = 1)\) (obs) | 0.0798 | 0.0796 | 0.0672 |
| \(R_F\) \((m = 2)\) (obs) | 0.2148 | 0.2119 | 0.0894 |
| \(wR_F\) \((m = 0)\) (all) | 0.0717 | 0.0717 | 0.0695 |
| \(wR_F\) \((m = 1)\) (all) | 0.0973 | 0.0972 | 0.0869 |
| \(wR_F\) \((m = 2)\) (all) | 0.3748 | 0.3721 | 0.1319 |
| \(wR_F\) all (all) | 0.0879 | 0.0877 | 0.0738 |
| GoF (obs/all) | 1.69/1.23 | 1.69/1.23 | 1.52/1.03 |
| \(\Delta \rho_{\text{min}}, \Delta \rho_{\text{max}}\) (e Å\(^{-3}\)) | -14.56, 14.53 | -14.52, 14.69 | -8.73, 6.14 |

Model A

Here, up to second-order harmonics have been applied to holmium and iridium atoms, whereas silicon atoms have only first-order harmonics (Eq. S6 in\(^\text{[10]}\)). This resulted in fewer parameters and minimal changes to the results as compared to models B and C (Table 2). This model has been selected to describe the crystal structure in the CDW phase.

Model B

In this model up to second-order displacement modulation parameters have been applied to all atoms and then refined. The refinement resulted in a fit to the SXRD data that is almost identical to that of Model A. However, the second-order modulation amplitudes of the silicon atoms appear to have large standard uncertainties (s.u.’s). This is probably due to the poor scattering power of silicon as compared to holmium or iridium. Together, these
features imply that the additional 30 parameters in model B do not lead to a significant improvement and model B is not selected.

**Model C**

Model C builds upon model A and model B in order to try solve the issue with the high value of $R_F$ for the second-order satellites. Up to third-order harmonics are used for the modulation functions of the holmium and iridium atoms, while employing only first-order harmonics for silicon atoms, as higher-order harmonics have been discarded for Si on the basis of models A and B. As a rule of thumb the highest harmonics in the modulation wave should not exceed the highest order of observed satellite reflections, the latter which is two in the present SXRD experiment. At first glance from Table 2 we see a huge improvement of the fit to the second-order satellites upon introduction of third-order harmonics. However, all these parameters have a s.u. that is larger than the refined value itself. The latter indicate that the system would have third-order satellite reflections with intensities larger than its first- and second-order satellites. As we did not observe third-order satellites, the refined values of the third-order harmonics appear to be unreliable, and model A is chosen in favor of model C.

**Location of the CDW**

Table S8 in the Supporting Information shows the atomic coordinates at 200 K and 70 K (warming). The six crystallographically independent atoms, Ho1, Ir1, Ir2, Si1, Si2, and Si3, of the *Ibam* structure at 200 K split into the Ho1a, Ho1b, Ir1a, Ir1b, Ir2, Si1, Si2a, Si2b, Si3a, Si3b atoms of the triclinic structure at 70 K. Figure 4 shows the crystal structure projected onto the a-c plane at 200 K and 70 K (average structure at 70 K). Figure 4(b) appears skew compared to Fig. 4(a) due to $\beta > 90$ deg in the CDW phase. As the modulation wave vector is close to (1/4, 1/2, 1/4), Fig. 4(c) shows a $4 \times 2 \times 4$ superstructure approximation, where one can see zigzag chains of Ir1a-Ir1b along c. Tables S9 and S10 in the Supporting
Information\textsuperscript{10} show the refined modulation amplitudes.

Figure 4: Projection onto the (a, c)-plane of the crystal structures of Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} for (a) 200 K and (b, c) 70 K. Panel (c) shows the $4 \times 2 \times 4$ superstructure approximation. Large purple spheres correspond to Ho atoms; green spheres of intermediate size correspond to Ir atoms; small yellow spheres are Si atoms. Dashed lines give the distances in the basic structure, with values of 3.390 (3) and 3.728 (3) Å.

Analysis of the modulation amplitudes and distances revealed that Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} follows a similar pattern as $R_2$Ir\textsubscript{3}Si\textsubscript{5} (Lu, Er),\textsuperscript{30,36} such that the CDW resides on zigzag chains of Ir1a-Ir1b atoms, as they have the shortest metal-metal distances and exhibit the largest modulation of these distances (Fig. 5). The lattice distortion results in alternating short and long Ir1a–Ir1b distances, where the shorter distance is the most affected by the modulation. The formation of dimers on the Ir1a-Ir1b zigzag chains along c is responsible for the formation of the CDW.

Table\textsuperscript{3} provides a comparison of essential structural parameters between the three compounds $R_2$Ir\textsubscript{3}Si\textsubscript{5}. Our earlier proposal, that $T_{CDW}$ would be inversely proportional to the atomic radius of the rare earth element, is not confirmed by Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5}. The atomic radius
of Ho is comparable to that of Er, however $T_{\text{CDW}}$ of Ho$_2$Ir$_3$Si$_5$ is much lower than that of Er$_2$Ir$_3$Si$_5$. The variation of distances Ir1a–Ir1b is more or less similar in all three compounds.

**Electronic structure and phonons**

The band structure of Ho$_2$Ir$_3$Si$_5$ is shown in Fig. 6(a) for several high-symmetry directions in the primitive BZ given in Fig. 6(b). It is metallic such that both electron and hole pockets exist at the Fermi level. To resolve the contributions of electronic states near the Fermi energy, we show the atomic orbital projected density of states (PDOS) in Fig. 6(c). The Ir states are dominant near $E_F$, whereas the Ho and Si states have lower weight than those of Ir atoms. To understand the charge density distributions of these atoms, we have shown the charge density on two different planes in the primitive unit cell, which contain Ho and Ir atoms, respectively [Figs. 6(d) and 6(e)]. The spherical charge distribution of these atoms is reminiscent of the metallic type ionic environment and suggests that these atoms are more likely to undergo CDW modulations to find a low energy state.

Figure 6(f) shows the phonon spectrum along various high-symmetry directions in the BZ. The system is dynamically unstable with Kohn-type soft modes at $Z$, $R$ and in be-
Table 3: Crystal data of the CDW phases of Lu$_2$Ir$_3$Si$_5$, Er$_2$Ir$_3$Si$_5$ and Ho$_2$Ir$_3$Si$_5$ (present results).

| Compound | Atomic radius of Lu$_2$Ir$_3$Si$_5$ | Er$_2$Ir$_3$Si$_5$ | Ho$_2$Ir$_3$Si$_5$ |
|----------|-----------------------------------|-------------------|-------------------|
|          | $R$ (Å)                           |                   |                   |
|          | 2.17                              | 2.26              | 2.26              |
| $T_{CDW}$ (K) | 202–231                          | 150–166           | 90–130            |
| $T$ (K)  | 60                                | 75                | 70                |
| $a$ (Å)  | 9.8182(3)                         | 9.8494(3)         | 9.8356(5)         |
| $b$ (Å)  | 11.4093(3)                        | 11.4863(3)        | 11.4902(4)        |
| $c$ (Å)  | 5.6835(2)                         | 5.7268(2)         | 5.7304(3)         |
| $\alpha$ (deg) | 90.001(2)                        | 90.079(1)         | 89.983(3)         |
| $\beta$ (deg) | 91.945(2)                        | 91.695(2)         | 91.772(2)         |
| $\gamma$ (deg) | 90.018(2)                        | 90.051(1)         | 89.975(1)         |
| $V$ (Å$^3$) | 636.34(3)                        | 647.60(5)         | 647.32(5)         |
| $q_x$    | 0.2499(3)                         | 0.2495(2)         | 0.2494(2)         |
| $q_y$    | 0.4843(4)                         | 0.4973(1)         | 0.4978(2)         |
| $q_z$    | 0.2386(2)                         | 0.2483(1)         | 0.2488(2)         |
| Distance Ir1a–Ir1b$^a$ |                                  |                   |                   |
| max (Å)  | 3.801(1)                          | 3.818(2)          | 3.801(3)          |
| min (Å)  | 3.711(1)                          | 3.714(2)          | 3.719(3)          |
| avg (Å)  | 3.755(1)                          | 3.764(2)          | 3.763(3)          |
| Distance Ir1a–Ir1b$^b$ |                                  |                   |                   |
| max (Å)  | 3.761(1)                          | 3.782(2)          | 3.728(3)          |
| min (Å)  | 3.002(1)                          | 3.008(2)          | 3.053(3)          |
| avg (Å)  | 3.385(1)                          | 3.398(2)          | 3.390(3)          |

$^a$Symmetry code for Ir1b $(x, y, z)$; given are the maximum (max), minimum (min) and average (avg) distances. $^b$Symmetry code for Ir1b $(x, y, z - 1)$. 
Figure 6: (a) Bulk electronic band structure of the orthorhombic phase of Ho$_2$Ir$_3$Si$_5$ along various high-symmetry directions in the primitive Brillouin zone. (b) Brillouin zone with high-symmetry points. (c) Total (highlighted grey color) and orbital projected density of states (green, red, and blue lines). (d) and (e) Electronic charge density distributions on planes containing Ho and Ir atoms, respectively. (f) Phonon band structure of the orthorhombic phase, as calculated with smearing parameter $\sigma = 0.05$ eV. (g) Phonon density of states. The imaginary frequencies are represented by negative values and are mainly associated with Ir atoms. (h) Expanded view of the phonon band structure along the $V$–$R$–$Y$ directions. The absence of imaginary frequencies for smearing parameter $\sigma = 0.5$ eV indicates the stability of the orthorhombic structure towards higher temperatures.
tween Y and U points. The phonon PDOS [Fig. 6(g)] shows that Ho and Ir atoms contribute to the low-frequency phonon modes, whereas high-frequency phonon modes are dominated by Si atoms. The imaginary frequencies are inherent to the Ir atoms, confirming that the CDW is associated mainly with the Ir atoms. The lowest value of negative frequency is found near the reciprocal point (0.25, 0.50, 0.25), which is consistent with the incommensurate wave vector \( \mathbf{q} \) found in the SXRD experiment. Figure 6(h) demonstrates the evolution of the soft phonon mode as a function of the smearing parameter \( \sigma \), which represents the electronic temperature in our calculations. The soft phonon mode disappears upon increasing the smearing parameter \( \sigma \) from 0.05 eV to 0.5 eV. This particular dependence of the phonon frequencies on the smearing parameter (electronic temperature) indicates that the orthorhombic structure is stable only at higher temperatures as seen in our experiments.

Electrical resistivity

Figure 7: Temperature dependence of the electrical resistivity \( \rho(T) \) of Ho\(_2\)Ir\(_3\)Si\(_5\). The pink and green regions indicate the periodic and CDW phases, respectively. A large hysteresis of 40 K is clearly seen. The crystal shattered on heating to above 130 K.

From Fig. 7 we infer that, upon cooling the crystal, there is a sharp upward turn of the electrical resistivity at 90 K, which signifies the opening of a gap in the electronic density of states over a major fraction of the Fermi surface, in agreement with the formation of a charge density wave (CDW) at this temperature. The metallic nature of the crystal after the CDW
transition indicates a partial opening of the gap at the Fermi surface. Upon heating, $\rho(T)$ shows a sharp anomaly at 130 K, thereby establishing a huge hysteresis of 90–130 K. This large hysteresis and the sharpness of the transition signify that it is a first-order transition much like the one seen in $R_2\text{Ir}_3\text{Si}_5$ ($R = \text{Lu, Er}$). Such a large hysteresis is uncommon for CDW transitions. Especially for incommensurate CDWs the transition usually is of second order, e.g. as found in the canonical CDW system NbSe$_3$.

All measurements were made using virgin samples. After cooling and then heating through the phase transition, micro-cracks develop due to the strain induced by the transition. This feature is visible in the electrical resistivity through a lower resistivity of virgin samples than of samples that have gone through a cooling/heating cycle (Fig. 7). Similar behavior has been observed for ceramic material of $R_2\text{Ir}_3\text{Si}_5$ ($R = \text{Lu, Er}$). It was explained by variations of pinning of the CDW in those systems. However, it is possible that the large lattice distortions accompanying the CDW transition could be responsible for the formation of micro-cracks. This leads to a reduction of sizes of mosaic blocks, and an increase in texture, which, in turn, would cause an increase of the electrical resistance at each thermal cycle. The presence of micro-cracks is supported by the observation that the transition temperatures and hysteresis are the same in each thermal cycle. On the other hand, the increase of pinning centers would lead to a lowering of the CDW transition temperature, which is not observed here. Just as in the case of $R_2\text{Ir}_3\text{Si}_5$ ($R = \text{Lu, Er}$), we observe that the electrical resistivity exhibits a $T^2$ dependence below $T = 50$ K, which is up to much higher temperatures than $\sim$10 K for a Fermi liquid, implying dominant contributions from short-range magnetic fluctuations of Ho spins in the absence of long-range magnetic ordering.

**Magnetic susceptibility**

The temperature-dependent magnetic susceptibility, $\chi(T)$, of Ho$_2$Ir$_3$Si$_5$ was measured on a single crystal from the same rod as used for the other bulk measurements. Measurements
were performed with a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS 7, Quantum Design, USA) employing a magnetic field of 0.1 T along c, during cooling and heating between 2 and 300 K (Fig. 8). The most interesting feature of the temperature-dependent magnetic susceptibility is the noticeable increase of $\chi(T)$ at 90(1) K upon cooling through the CDW transition. The observed effect cannot be explained by a change of Pauli susceptibility at the transition, since the estimated magnitude of the Pauli susceptibility is at least two orders of magnitude smaller than the observed change in the susceptibility. Furthermore, one would expect a smaller Pauli susceptibility in the CDW phase, whereas we observe an increase of the susceptibility when cooling through the transition. The same transition is found at 130(1) K upon heating. The observed hysteresis is in good agreement with the hysteresis in the electrical resistivity and DSC measurements. A Curie-Weiss fit to the data at 140–300 K results in a Curie constant of $C = 31.78(1)$ emu/mol K and an antiferromagnetic Weiss temperature of $\theta = -2.6(1)$ K. A Curie-Weiss fit to the low-temperature paramagnetic regime 40–90 K results in $C = 32.4(1)$ emu/mol K and $\theta = -6.3(1)$ K. The different Curie constants correspond to different effective magnetic moments on Ho$^{3+}$ of 11.27 $\mu_B$ and 11.38 $\mu_B$, respectively. These values are slightly higher than the free ion magnetic moment of Ho$^{3+}$ ions.
So we see that Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} joins our earlier studied Er\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5}\textsuperscript{20} as yet another exceptional case in showing an effect of the CDW transition on the magnetic susceptibility. Usually, compounds containing magnetic rare-earth elements do not show any anomaly in the paramagnetic susceptibility at the high-temperature CDW transitions. This is true for many of the magnetic CDW compounds which are mentioned in the introduction. For example, the paramagnetic susceptibility of Ho\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10} does not show any anomalies at its CDW transition.\textsuperscript{56,57} The coexistence of antiferromagnetic order ($T_N = 2$ K) and CDW in Ho\textsubscript{5}Ir\textsubscript{4}Si\textsubscript{10} might be related to the presence of weakly coupled 4$f$ electrons of Ho\textsuperscript{3+} ions,\textsuperscript{15} while for Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} the reduced magnitude of the magnetic moments and strong coupling suggest influence of the 4$f$ electrons in the CDW transition and vice versa. It is not clear, whether the small but distinct change of Ho\textsuperscript{3+} moment (11.27 $\mu_B$ vs 11.38 $\mu_B$) across the CDW transition in a single crystal of Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} could be responsible for the absence of magnetic ordering of Ho\textsuperscript{3+} moments in the crystal down to 2 K.

**Specific heat**

![Figure 9: Temperature dependence of the specific heat $C_p$ from 2 to 250 K using PPMS. The inset provides an enlarged view of the CDW transition where $\Delta C_p = 60.5(1)$ J/(mol K).](image)

The specific heat ($C_p(T)$) of Ho\textsubscript{2}Ir\textsubscript{3}Si\textsubscript{5} was measured by the thermal relaxation method, using a physical property measuring system (PPMS, Quantum Design, USA). Data obtained
Figure 10: Temperature dependence of the excess specific heat $\Delta C_p$, obtained by subtracting a smooth baseline from the DSC signal. Blue and red circles refer to cooling and warming data. Clear peaks are observed in both cooling and warming with a hysteresis of about 40 K.

During heating of a single crystal of 10.5 mg from 2 to 250 K exhibit a sharp peak at the temperature of the CDW transition at 131.1 (1) K (Fig. 9). We are unable to find a peak in $C_p(T)$ while cooling the crystal. Similar behavior was noted earlier for a crystal of Lu$_2$Ir$_3$Si$_5$. This feature could be the result of the specific method of measurement employed in the PPMS instrument. In a second experiment, differential scanning calorimetry (DSC) was measured from 80 to 150 K on the same single crystal of Ho$_2$Ir$_3$Si$_5$ (Fig. 10). The DSC data show clear peaks at different temperatures in the heating and cooling runs, that appear at similar temperatures as are found for the electrical resistivity and magnetic susceptibility, and thus confirm the first-order character of the phase transition. The peaks appear of similar width as for Lu$_2$Ir$_3$Si$_5$ while the DSC peaks are much sharper for Er$_2$Ir$_3$Si$_5$. Since other features, like $C_p(T)$ and $\rho(T)$, exhibit very sharp anomalies at the CDW transition, the broadened features in the DSC signal might be related to the rate of change of temperature in this experiment in conjunction with the sluggish character of the transition.

The lattice contribution to the specific heat was determined from a fit to the data far away from the transition. Subtraction of the lattice contribution resulted in $\Delta C_p(T)$ (inset in Fig. 9). A similar value was obtained from the DSC measurement (Fig. 10).
change of entropy at the transition $\Delta S$ has been determined by integration of $\frac{\Delta C_p(T)}{T}$ over temperature. The values of $\Delta C_p = 60.5(1)$ J/(mol K) and $\Delta S = 0.6$ J/mol are comparable to transition entropies for $R_5$Ir$_3$Si$_{10}$ and $R_2$Ir$_3$Si$_5$. However, they are much larger than obtained for conventional CDW systems, such as K$_{0.3}$MoO$_3$ ($\Delta C_p$(max) = 8 J/(mol K); $\Delta S = 0.18R$) and NbSe$_3$ ($\Delta C_p$(max) = 9 J/(mol K); $\Delta S = 0.08R$). The specific heat anomaly indicates a much sharper transition for single crystals of Ho$_2$Ir$_3$Si$_5$ than for conventional CDW systems, which is in agreement with the first-order character of the transition as deduced from resistivity and magnetic susceptibility data.

**Conclusions**

We have established an incommensurately modulated crystal structure of the CDW phase of Ho$_2$Ir$_3$Si$_5$. The incommensurate modulation is accompanied by a strong lattice distortion, both of which are important for the modulation of interatomic distances on zigzag chains of iridium atoms along $c$. This is in accordance with the CDW being supported by these zigzag chains. Similar to the case of Er$_2$Ir$_3$Si$_5$, the rare earth atoms are not directly involved in the CDW formation. The occurrence of a large lattice distortion accounts for the sluggish character and large hysteresis of the transition, as they are apparent in the temperature dependencies of the electrical resistivity, magnetic susceptibility and specific heat. Another unique feature of the compounds $R_2$Ir$_3$Si$_5$ ($R = $ Lu, Er and Ho) is the extreme sensitivity of the phase transitions to crystalline order. The present single crystals of high perfection undergo a CDW transition, while magnetic order is suppressed down to at least 1.5 K. It is worthwhile to point out that the previous experiments on polycrystalline material did not observe the CDW transition, while magnetic order appeared below $T_N = 5.1$ K. The present results on Ho$_2$Ir$_3$Si$_5$ do not confirm the idea that $T_{CDW}$ would scale with the atomic radius of the rare earth element. While the size of Ho is equal to that of Er, $T_{CDW}$ is much lower for Ho$_2$Ir$_3$Si$_5$ than for Er$_2$Ir$_3$Si$_5$. This absence of a correlation in the series $R_2$Ir$_3$Si$_5$
is in contrast to the series of isostructural rare-earth compounds $R_5\text{Ir}_4\text{Si}_{10}$, where $T_{CDW}$ increases with increasing size of the rare earth element $R$.

The SXRD data have revealed that the structure of Ho$_2$Ir$_3$Si$_5$ is different from that of Lu$_2$Ir$_3$Si$_5$ and Er$_2$Ir$_3$Si$_5$. Although the symmetries are the same for all three compounds, the presence of second-order superlattice reflections in the CDW phase of Ho$_2$Ir$_3$Si$_5$ has added more complexity to it, requiring modulation functions with up to second-order harmonics (model A in Section ).

From physical property measurements, a huge hysteresis is found of about 40 K, with the transition proceeding at 90 K (cooling) and 130 K (warming). The transition implies severe structural distortions, such that sometimes the crystal shatters. This is visible in the electrical resistivity, which is higher after cycling though the transition than before (Fig. 7). The effective magnetic moment of Ho is found to change at the CDW transition, from 11.38 $\mu_B$ to 11.27 $\mu_B$ (Fig. 8). This kind of coupling between CDW and magnetism is rare. It has only been observed in isostructural Er$_2$Ir$_3$Si$_5$. This feature can probably be attributed to the participation of 4f orbitals of Ho or Er in states near the Fermi level that are involved in CDW ordering. The fact the effective moment of the rare earth is influenced by the CDW transition suggests a competition between CDW and magnetic order, with both interactions presumably employing the same part of the Fermi surface. In order to clearly understand the mechanism for this unusual nature one would probably need microscopic probes of magnetism, such as elastic and inelastic neutron scattering.

**Acknowledgement**

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. J.-K. Bao acknowledges financial support from the Alexander-von-Humboldt foundation. The work at TIFR Mumbai was supported by the Department of
Atomic Energy of the Government of India under Project No. 12-R&D-TFR-5.10-0100. This research has been funded by the Deutsche Forschungsgemeinschaft (DFG; German Research Foundation)–406658237.

Supporting Information Available

Details of the SXRD data collection, data processing and structural analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Grüner, G. Charge Density Waves in Solids; Addison-Wesley: Reading, Massachusetts, 1994.

(2) Marmeggi, J. C.; Delapalme, A.; Lander, G. H.; Vettier, C.; Lehner, N. Atomic displacements in the incommensurable charge-density wave in alpha-uranium. Sol. Stat. Commun. 1982, 43, 577–581.

(3) Fleming, R. M.; DiSalvo, F. J.; Cava, R. J.; Waszczak, J. V. Observation of Charge-Density waves in the cubic spinel structure CuV$_2$S$_4$. Phys. Rev. B 1981, 24, 2850–2853.

(4) Kawaguchi, S.; Kubota, Y.; Tsuji, N.; Kim, J.; Kato, K.; Takata, M.; Ishibashi, H. Structural Analysis of Spinel Compound CuV$_2$S$_4$ with Incommensurate Charge-Density Wave. J. Phys. Conf. Ser. 2012, 391, 012095.

(5) Okada, H.; Koyama, K.; Watanabe, K. Two-Step Structural Modulations and Fermi Liquid State in Spinel Compound CuV$_2$S$_4$. J. Phys. Soc. Jpn 2004, 73, 3227–3230.

(6) Ramakrishnan, S.; Schönleber, A.; Hübschle, C. B.; Eisele, C.; Schaller, A. M.; Rekis, T.; Bui, N. H. A.; Feulner, F.; van Smaalen, S.; Bag, B.; Ramakrishnan, S.;
Tolkiehn, M.; Paulmann, C. Charge density wave and lock-in transitions of CuV$_2$S$_4$. 
*Phys. Rev. B* **2019**, *99*, 195140.

(7) Ślebarski, A.; Goraus, J. Electronic structure and crystallographic properties of skutterudite-related Ce$_3$M$_4$Sn$_{13}$ and La$_3$M$_4$Sn$_{13}$ ($M$ = Co, Ru, and Rh). *Phys. Rev. B* **2013**, *88*, 155122.

(8) Otomo, Y.; Iwasa, K.; Suyama, K.; Tomiyasu, K.; Sagayama, H.; Sagayama, R.; Nakao, H.; Kumai, R.; Murakami, Y. Chiral crystal-structure transformation of R$_3$Co$_4$Sn$_{13}$ ($R$ = La and Ce). *Phys. Rev. B* **2016**, *94*, 075109.

(9) Welsch, J.; Ramakrishnan, S.; Eisele, C.; van Well, N.; Schönleber, A.; van Smaalen, S.; Mattepanavar, S.; Thamizhavel, A.; Tolkiehn, M.; Paulmann, C.; Ramakrishnan, S. Second-order charge-density-wave transition in single crystals of La$_3$Co$_4$Sn$_{13}$. *Phys. Rev. Materials* **2019**, *3*, 125003.

(10) DiMasi, E.; Aronson, M. C.; Mansfield, J. F.; Foran, B.; Lee, S. Chemical pressure and charge-density waves in rare-earth tritellurides. *Phys. Rev. B* **1995**, *52*, 14516–14525.

(11) Ru, N.; Condron, C. L.; Margulis, G. Y.; Shin, K. Y.; Laverock, J.; Dugdale, S. B.; Toney, M. F.; Fisher, I. R. Effect of chemical pressure on the charge density wave transition in rare-earth tritellurides RTe$_3$. *Phys. Rev. B* **2008**, *77*, 035114.

(12) Banerjee, A.; Feng, Y.; Silevitch, D. M.; Wang, J.; Lang, J. C.; Kuo, H.-H.; Fisher, I. R.; Rosenbaum, T. F. Charge transfer and multiple density waves in the rare earth tellurides. *Phys. Rev. B* **2013**, *87*, 155131.

(13) DiMasi, E.; Foran, B.; Aronson, M. C.; Lee, S. Stability of charge-density waves under continuous variation of band filling in LaTe$_{2-x}$Sb$_x$ ($0 < x < 1$). *Phys. Rev. B*. **1996**, *54*, 13587–13596.
(14) Shim, J. H.; Kang, J.-S.; Min, B. I. Electronic Structures of $R$Te$_2$ ($R =$ La, Ce): A Clue to the Pressure-Induced Superconductivity in CeTe$_{1.82}$. Phys. Rev. Lett. 2004, 93, 156406.

(15) Ramakrishnan, S.; van Smaalen, S. Unusual ground states in $R_5T_4X_{10}$ ($R =$ rare earth; $T =$ Rh, Ir; and $X =$ Si, Ge, Sn): a review. Rep. Prog. Phys. 2017, 80, 116501.

(16) Kuo, C. N.; Hsu, C. J.; Tseng, C. W.; Chen, W. T.; Lin, S. Y.; Liu, W. Z.; Kuo, Y. K.; Lue, C. S. Charge density wave like behavior with magnetic ordering in orthorhombic Sm$_2$Ru$_3$Ge$_5$. Phys. Rev. B 2020, 101, 155140.

(17) Nakamura, A.; Uejo, T.; Honda, F.; Takeuchi, T.; Harima, H.; Yamamoto, E.; Haga, Y.; Matsubayashi, K.; Uwatoko, Y.; Hedo, M.; Nakama, T.; Onuki, Y. Transport and Magnetic Properties of EuAl$_4$ and EuGa$_4$. J. Phys. Soc. Jpn 2015, 84, 124711.

(18) Shimomura, S.; Murao, H.; Tsutsui, S.; Nakao, H.; Nakamura, A.; Hedo, M.; Nakama, T.; Onuki, Y. Lattice Modulation and Structural Phase Transition in the Antiferromagnet EuAl$_4$. J. Phys. Soc. Jpn 2019, 88, 014602.

(19) Kaneko, K.; Kawasaki, T.; Nakamura, A.; Munakata, K.; Nakao, A.; Hanashima, T.; Kiyanagi, R.; Ohhara, T.; Hedo, M.; Nakama, T.; Onuki, Y. Charge-Density-Wave Order and Multiple Magnetic Transitions in Divalent Europium Compound EuAl$_4$. J. Phys. Soc. Jpn 2021, 90, 064704.

(20) Ramakrishnan, S. et al. Orthorhombic charge density wave on the tetragonal lattice of EuAl$_4$. IUCrJ 2022, 9, 378–385.

(21) Meier, W. R.; Torres, J. R.; Hermann, R. P.; Zhao, J.; Lavina, B.; Sales, B. C.; May, A. F. Thermodynamic insights into the intricate magnetic phase diagram of EuAl$_4$. Phys. Rev. B 2022, 106, 094421.
(22) Zeng, L.; Hu, X.; Wang, N.; Sun, J.; Yang, P.; Boubeche, M.; Luo, S.; He, Y.; Cheng, J.; Yao, D.-X.; Luo, H. Interplay between Charge-Density-Wave, Superconductivity, and Ferromagnetism in CuIr$_{2-x}$Cr$_x$Te$_4$ Chalcogenides. J. Phys. Chem. Lett. 2022, 13, 2442–2451.

(23) Roman, M.; Strychalska-Nowak, J.; Klimczuk, T.; Kolincio, K. K. Extended phase diagram of RNiC$_2$ family: Linear scaling of the Peierls temperature. Phys. Rev. B 2018, 97, 041103(R).

(24) Shimomura, S.; Hayashi, C.; Asaka, G.; Wakabayashi, N.; Mizumaki, M.; Onodera, H. Charge-Density-Wave Destruction and Ferromagnetic Order in SmNiC$_2$. Phys. Rev. Lett. 2009, 102, 076404.

(25) Wölfel, A.; Li, L.; Shimomura, S.; Onodera, H.; van Smaalen, S. Commensurate charge-density wave with frustrated interchain coupling in SmNiC$_2$. Phys. Rev. B 2010, 82, 054120.

(26) Shimomura, S.; Hayashi, C.; Hanasaki, N.; Ohnuma, K.; Kobayashi, Y.; Nakao, H.; Mizumaki, M.; Onodera, H. Multiple charge density wave transitions in the antiferromagnets RNiC$_2$ ($R = $ Gd, Tb). Phys. Rev. B 2016, 93, 165108.

(27) Kolincio, K. K.; Roman, M.; Winiarski, M. J.; Strychalska-Nowak, J.; Klimczuk, T. Magnetism and charge density waves in RNiC$_2$ ($R = $ Ce, Pr, Nd). Phys. Rev. B 2017, 95, 235156.

(28) Maeda, H.; Kondo, R.; Nogami, Y. Multiple charge density waves compete in ternary rare-earth nickel carbides, RNiC$_2$ ($R$: Y, Dy, Ho, and Er). Phys. Rev. B 2019, 100, 104107.

(29) Kolincio, K. K.; Roman, M.; Klimczuk, T. Enhanced Mobility and Large Linear Non-saturating Magnetoresistance in the Magnetically Ordered States of TmNiC$_2$. Phys. Rev. Lett. 2020, 125, 176601.
(30) Ramakrishnan, S.; Schönleber, A.; Rekis, T.; van Well, N.; Noohinejad, L.; van Smaalen, S.; Tolkiehn, M.; Paulmann, C.; Bag, B.; Thamizhavel, A.; Pal, D.; Ramakrishnan, S. Unusual charge density wave transition and absence of magnetic ordering in Er$_2$Ir$_3$Si$_5$. *Phys. Rev. B* **2020**, *101*, 060101(R).

(31) Sangeetha, N. S.; Thamizhavel, A.; Tomy, C. V.; Basu, S.; Awasthi, A. M.; Rajak, P.; Bhattacharyya, S.; Ramakrishnan, S.; Pal, D. Multiple charge density wave transitions in single-crystalline Lu$_2$Ir$_3$Si$_5$. *Phys. Rev. B* **2015**, *91*, 205131.

(32) Singh, Y.; Pal, D.; Ramakrishnan, S. Low-temperature studies of the magnetic and superconducting properties of the $R_2$Ir$_3$Si$_5$ ($R$ = Y, La, Ce–Nd, Gd–Tm) system. *Phys. Rev. B* **2004**, *70*, 064403.

(33) Singh, Y.; Pal, D.; Ramakrishnan, S.; Awasthi, A. M.; Malik, S. K. Phase transitions in Lu$_2$Ir$_3$Si$_5$. *Phys. Rev. B* **2005**, *71*, 045109.

(34) Kuo, Y. K.; Sivakumar, K. M.; Su, T. H.; Lue, C. S. Phase transitions in Lu$_2$Ir$_3$Si$_5$: An experimental investigation by transport measurements. *Phys. Rev. B* **2006**, *74*, 045115.

(35) Lee, M. H.; Chen, C. H.; Chu, M.-W.; Lue, C. S.; Kuo, Y. K. Electronically phase-separated charge-density waves in Lu$_2$Ir$_3$Si$_5$. *Phys. Rev. B* **2011**, *83*, 155121.

(36) Ramakrishnan, S.; Schönleber, A.; Bao, J.-K.; Rekis, T.; Kotla, S. R.; Schaller, A. M.; van Smaalen, S.; Noohinejad, L.; Tolkiehn, M.; Paulmann, C.; Sangeetha, N. S.; Pal, D.; Thamizhavel, A.; Ramakrishnan, S. Modulated crystal structure of the atypical charge density wave state of single-crystal Lu$_2$Ir$_3$Si$_5$. *Phys. Rev. B* **2021**, *104*, 054116.

(37) Clementi, E.; Raimondi, D. L.; Reinhardt, W. P. Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons. *J. Chem. Phys.* **1967**, *47*, 1300.

(38) Meier, W. R.; Chakoumakos, B. C.; Okamoto, S.; McGuire, M. A.; Hermann, R. P.;
Samolyuk, G. D.; Gao, S.; Zhang, Q.; Stone, M. B.; Christianson, A. D.; Sales, B. C. A Catastrophic Charge Density Wave in BaFe$_2$Al$_9$. *Chem. Mater.* **2021**, *33*, 2855–2863.

(39) Stokes, H. T.; Campbell, B. J.; van Smaalen, S. Generation of (3 + d)-dimensional superspace groups for describing the symmetry of modulated crystalline structures. *Acta Crystallogr. A* **2011**, *67*, 45–55.

(40) See Supplemental Material at [URL will be inserted by publisher] for details on the diffraction experiments and values of the structural parameters.

(41) Schreurs, A. M. M.; Xian, X.; Kroon-Batenburg, L. M. J. EVAL15: a diffraction data integration method based on ab initio predicted profiles. *J. Appl. Crystallogr.* **2010**, *43*, 70–82.

(42) Sheldrick, G. M. *SADABS, Version 2008/1*; Göttingen: University of Göttingen, 2008.

(43) van Smaalen, S. *Incommensurate Crystallography*; International Union of Crystallography Monographs on Crystallography; OUP Oxford, 2007.

(44) Wagner, T.; Schönleber, A. A non-mathematical introduction to the superspace description of modulated structures. *Acta Crystallogr. B* **2009**, *65*, 249–268.

(45) Petricek, V.; Eigner, V.; Dusek, M.; Cejchan, A. Discontinuous modulation functions and their application for analysis of modulated structures with the computing system JANA2006. *Z. Kristallogr.* **2016**, *231*, 301–312.

(46) Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic computing system JANA2006: general features. *Z. Kristallogr.* **2014**, *229*, 345–352.

(47) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(48) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
(50) Momma, K.; Izumi, F. VESTA: a three-dimensional visualization system for electronic and structural analysis. *J. Appl. Crystallogr.* **2008**, *41*, 653–658.

(51) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scripta Mater.* **2015**, *108*, 1–5.

(52) Parsons, S. Introduction to twinning. *Acta Crystallogr. Section D* **2003**, *59*, 1995–2003.

(53) Bartl, H.; Schuster, D.; Schroeder, F. A. Verfeinerung der Kristallstruktur der blauen Kalium Molybdaen-bronze, $\text{K}_{0.3}\text{MoO}_3$, durch Roentgenbeugung. *Zeitschrift fur Kristallographie* **1979**, *149*, 127–128.

(54) Kohn, W. Image of the Fermi Surface in the Vibration Spectrum of a Metal. *Phys. Rev. Lett.* **1959**, *2*, 393–394.

(55) Tomić, S.; Biljaković, K.; Djurek, D.; Cooper, J.; Monceau, P.; Meerschaut, A. *Solid State Commun.* **1981**, *38*, 109–112.

(56) Yang, H. D.; Klavins, P.; Shelton, R. N. Low-temperature physical properties of $R_5\text{Ir}_4\text{Si}_{10}$ ($R = \text{Dy, Ho, Er, Tm, and Yb}$) compounds. *Phys. Rev. B* **1991**, *43*, 7688–7694.

(57) Ghosh, K.; Ramakrishnan, S.; Chandra, G. Magnetism in the $R_5\text{Ir}_4\text{Si}_{10}$ ($R = \text{Ho and Er}$) systems. *Phys. Rev. B* **1993**, *48*, 4152–4155.
Graphical TOC Entry