Supporting Information

Twisting of 2D kagomé sheets in layered intermetallics

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EXPERIMENTAL SECTION

A. Characterization

For single crystal X-ray diffraction (SXRD) all reflection intensities were measured at T = 100(2) K and 293(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo-Kα radiation (λ = 0.71073 Å) using the program CrysAlisPro (version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The crystal structures were solved in WinCIX and refined with the program SHELXS-2008 [1]. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). Electron diffraction images were collected using a Phillips CM300 atomic resolution Transmission Electron Microscope (TEM) equipped with a Field Emission Gun with an accelerating voltage of 300 kV. The selected area electron diffraction (SAED) patterns were taken from crushed crystals suspended in acetone on a carbon-coated Cu grid. A Quantum Design Physical Properties Measurement System (PPMS) was used for the heat capacity measurements from T ~ 1.9 to 300 K at μμH = 0 T using the semi-adiabatic method and a 1% temperature rise. Resistivity was conducted by four-probe method in the PPMS from T ~ 1.9 to 300 K at μμH = 0 T using silver paint to attach the leads to the sample which could be done easily on the large single crystals and the magnetization measurements were done at μμH = 1 T in the same temperature range. 3D Micro-Computed Tomography (CT) data was collected using a Bruker SkyScan 1172 with the X-ray source set to 80 kV/124 Å. Frames were collected in 0.1° steps over 180° using an Al/Cu filter and a SHT 11 MP camera, averaging 10 frames per step and 3400 ms of exposure per step. 3D reconstruction was performed using NRecon software with smoothing, ring artifact correction, and beam hardening correction applied. Data were visualized using Dragonfly software by ORS. Density Functional Theory (DFT) calculations were performed with an all-electron full-potential linearized augmented-plane wave basis with local orbitals as implemented in Elk (Electrons in K-Space)[2]. All data were processed using Origin 2020 and structures were visualized using the Vesta software [3]. Using Quantum Espresso (QE) [4] with projector-augmented wave (PAW) method and Perdew-Burke-Ernzerhof (PBE) exchange-correlations, ground-state calculations were performed on the compound. Local Orbital Basis Suite Toward Electronic Structure Reconstruction (LOBSTER) software processes the output data from QE to analyze chemical-bonding. The band structure energy is partitioned into bonding, nonbonding, and antibonding contributions to calculate crystal orbital Hamilton population (COHP)[5-8]. The room temperature structure was transformed into low temperature cell settings using ISODISTORT software [9,10].

RESULTS AND DISCUSSION

A. Single Crystal Structure

SXRD precession images were examined to understand the single crystal structure of MgCoGe₆. Trying to index the peaks in the precession images obtained at T = 100(2) K from the single crystals of MgCoGe₆ in the same space group as previously reported [11] resulted in unindexed peaks. All the reflections could be accounted for by doubling the unit cell along c axis (Fig 1b) and reducing the diffraction data in P6/mcm (Space group 193). The reflections corresponding to t = 2n + 1 are absent which is consistent to the new space group. No visible signs of phase transitions were observed on heating the system. No twinning was observed in any of the diffraction images. Structure solution obtained from the refinement to the SXRD data collected at T = 100(2) K on a single crystal of MgCoGe₆ shows no systematic absence violations in P6/mcm, while the higher temperature structure was found to be P6/mmm. The low temperature structure shows doubling of the unit cell along c axis agreeing with the analyses of the precession images. A displacive disorder modelled by the movement of the partial atoms by one-fourth of the unit cell along c axis accompanied by Mg vacancies was found in the structure (Fig 1d). Initial attempts to model the SXRD data of MgCoGe₆ at T = 293(2) K with the HfFe₆Ge₆ structure resulted in R₁ = 1.93%, wR₂ = 5.63%, y² = 1.615, with unaccounted residual electron density in between Mg and Ge₃ atoms along c axis. Similar residual electron density observed in neutron powder diffraction studies on TbCr₆Ge₆ has been interpreted as a partially disordered variant of hexagonal HfFe₆Ge₆ structure type (P6/mmm) where the Tb-(Ge2)-Tb-(Ge2) chains are shifted by half a unit cell along the c axis [12]. Such disorder would explain the observed excess density in the MgCo₆Ge₆; quantitative attempts at refinement gave R₁ = 1.46%, wR₂ = 4.16%, y² = 1.163, but with negative scattering holes in the positions of the displaced Mg ions; removing the Mg ions gave an improved fit to the data, R₁ = 1.31%, wR₂ = 3.47%, y² = 1.262, with a refined fraction of the translated fraction of ~5%. We thus conclude that ~5% Mg vacancies, expected on thermodynamic grounds given the volatility of Mg, generate columnar disorder in MgCo₆Ge₆ by introducing localized changes in the Ge₃-Ge₃ stacking along c axis. Similar disorder was found while modelling the low temperature structure as well. The covalent bond distance between the Ge₃-Ge₃ atoms in the majority component is ~ 2.49 Å which is considerably shorter than the Ge₃-Ge₃ distance in the graphene layers (2.94(12) Å) and indicative of strong Ge-Ge pair formation due to electron donation from the electropositive Mg⁺. The disorder accompanied by the absence of Mg²⁺ helps the Ge₃-Ge₃ bonds to relax to ~ 3.05 Å. No such disorder was observed in the single crystals of LaFe₆Ge₆ and YCr₆Ge₆ (Table SVI–IX) possibly due to less volatility of Lu and Y compared to Mg. This type of disorder is analogous to normal and collapsed structures in planar AB₃X₂ systems. An ideal example in planar AB₃X₂ systems is the pressure-tunable P-P bond distance between SrRh₂P₂ (3.284 Å) and SrPd₂P₂ (2.217 Å) [13].
B. Curie-Weiss Analysis

Initially analysis was performed using the Curie-Weiss law. The Curie constant provided by the analysis is 0.006 emu·K⁻¹·Oe⁻¹ for the parallel measurement, where the expected values are 0.37 or 1.87 for a $S = 1/2$ or $S = 3/2$ system, respectively. This analysis indicates that the observed behavior most likely results from impurity spins from surface oxides due to the small magnetic moment. Delocalized electrons can also contribute to magnetic susceptibility as a response to the magnetic field, resulting from Pauli paramagnetism which is indicative of metallic behavior.

C. Low temperature Einstein phonon mode

The small feature around $T \sim 3.7$ K is the superconducting transition from the minor amount of leftover Sn flux on the YCr₆Ge₆ crystal. To obtain the electronic contribution ($\gamma$) for a material the heat capacity data can be modelled to fit equation:

$$C_p = \gamma T + \beta_3 T^3 + \beta_5 T^5 + \beta_7 T^7 \approx \gamma T + \beta_3 T^3$$

where at low temperatures ($T \ll \theta_D/50$) the higher order terms can be ignored to obtain the value of electronic contribution by a linear fit to the $C_p/T$ vs $T^2$ plot (Fig S1b). After subtracting the electronic contribution ($\gamma$) (Fig S1b) from the bulk specific heat we try to model the data to reflect the behaviour of the one-dimensional phonon density of states (Fig 3) [14]. In this model, the Debye (acoustic) contribution is represented by a constant up to $\theta_D$, whereas an Einstein (optical) mode is represented by a peak, resulting from activated low T behaviour. The most striking feature of the plot is a low temperature peak at $T \sim 25$ K with $\theta_D = 121.4(47)$ K, indicating the data cannot be described by any combination of Debye terms (Table SX). The data below $T \sim 10$ K is noisy after the subtraction of the huge electronic contribution from the specific heat. The high energy part of the spectrum in MgCo₆Ge₆ was fit with a Debye contribution having $\theta_D = 363(1)$ K. The $\theta_D$ goes down to 336(1) K in YCr₆Ge₆ possibly due to less coupling of the higher mass Y with the Ge atoms compared to Mg. In the LuFe₆Ge₆ crystals we observe two Debye modes at $\theta_D = 246(3)$ K and $\theta_D = 591(26)$ K further confirming the decoupling of the atoms with increasing difference in masses between them. While the low-lying Einstein peak can be described by the vibrations of the local modes, the high temperature Debye mode is associated with higher energy vibrations of atoms having lower masses. Inversely, the lower temperature Debye mode is associated with lower energy vibrations of atoms having higher atomic masses. The total number of oscillators for each of the fits sum to ~ 13 (the number of atoms per formula unit) agreeing well with the theoretical value. No evidence of excess low temperature Einstein phonon modes was observed in YCr₆Ge₆ and LuFe₆Ge₆ supporting the origins as tied to local disorder in the structure. Efforts to fit an Einstein mode in the LuFe₆Ge₆ data resulted in the deviation of the total number of oscillators from ~13. Further, we did not observe any possible phase transitions in any of the single crystals.

D. Interlayer bonding and pairwise buckling of layers in 2D systems

Interlayer Au-Au bonded Au-Sb layers in LnAuSb ($Ln = $ La-Nd, Sm)

The YPt₆-type LnAuSb family is one of the characteristic examples of buckling of the planar lattice of Au-Sb atoms (Fig 5c) to create interplanar Au-Au bonds which is responsible for chemical stability of the compound [15]. The Au-Au dimers host one electron per Au to make these unique 111 hexagonal systems stable with 19 valence electron count. The Half-Heusler and hexagonal compounds (AYZ) show a varied range of Y-Z, Y-Y, Z-Z bonds in between the honeycomb layers [16-18]. In LnAuSb phases the neighboring honeycomb layers alternate in …YYZYYZZ…stacking order which favors pairwise interlayer bonding between similar atoms.

2D Van der Waals Layered Trimerized Kagomé Magnet – Nb₃Cl₆

NbCl₆ layered halide structures consist of NbCl₃: clusters composed of three edge-sharing NbCl₆ octahedra meeting at an apical Cl atom atop the Nb₃ triangle [19,20]. The high temperature ($T \approx 300$ K) structure solved in $P-3m$ shows stacking of two different types of layers. The low temperature structure shows monoclinic $C2/m$ symmetry with the breaking of $C\gamma$ symmetry of NbCl₃: clusters from high temperature to low temperature ($T \approx 10$ K) structure. This is consistent with second order Jahn-Teller distortion (SOJT) resulting in change in the stacking order of the layers. This change in the stacking order is attributed to buckling of Cl layers due to an inter-layer electronic interaction and SOJT distortion combined with singlet formation. Fig 5a shows the buckling of Cl layers in pairs along c axis followed by a pair of planar Cl layers.

LiZnGe structure type

LiZnGe crystallizes in the non-centrosymmetric space group $P-6m2$ [19] with a structure consisting of 2D layers of ZnGe with Li cations sandwiched between them. One of the characteristic features of this structure being interlayer bonding between Zn-Ge (2.76(1) Å) and Ge-Ge atoms (2.56(1) Å). This leads to the buckling of the layers in pairs (Fig 5b). Another similar example is the intermetallic germanides of $\alpha$-CaZnGe ($P\bar{6}m/m$) and $\beta$-CaZnGe ($P-6m2$). Unlike $\alpha$-CaZnGe ($P\bar{6}m/m$) its structural polymorph $\beta$-CaZnGe shows similar structure type as LiZnGe ($P-6m2$). The key difference between the two polymorphs being the pair-wise distortion of the honeycomb lattices. No distortion in the ZnGe layers are observed in the $\alpha$-CaZnGe ($P\bar{6}m/m$) structure, on the other hand the $\beta$-CaZnGe ($P-6m2$) structure features one planar anionic layer followed by a pair of puckered anionic layers of ZnGe along the c axis. Although the increase in cationic size from Li to Ca increases the interlayer distance making the Zn-Ge (4.097 Å) and Ge-Ge (4.563 Å) distances unreasonable for strong bonding interactions the COHP calculations reported by Zhu et al. indicate that the Zn-Ge interactions should still be treated as covalent bonds [21]. This unique feature leads to excellent electrical as well as low thermal conductivity.
E. Calculation:

Wilson Ratio ($K_w$) [22]

\[
K_w = \frac{\left(\pi^2 k_B^2 \chi\right)}{3 \mu B^2 \gamma}
\]

Where is $k_B$ Boltzmann constant,

$\mu B$ is Bohr Magneton,

$\chi$ is Pauli susceptibility and $\gamma$ is Sommerfield coefficient.

$\gamma = 20.84(28) \text{ mJ.K}^{-2}.\text{mol}^{-1}$ from heat capacity fit [Fig 6].

$\chi_{\Gamma-o} = 0.0022 \text{ emu.Oe}^{-1}.\text{mol}^{-1}$ (perpendicular to field direction).

Putting these values,

$K_w \sim 7.68 \text{ (Perpendicular to field direction).}$

$\sim 5.23 \text{ (Parallel to the field direction).}$

F. Electronic structure in MT$_6$X$_6$ Kagomés

We explore the band structures of the synthesized kagomé compounds to understand the correlation of the physical properties with the electronic structure. We computed the electronic band structures of MgCo$_6$Ge$_6$, YCr$_6$Ge$_6$, and LuFe$_6$Ge$_6$ (Fig S5a, b, c) at room temperatures. YCr$_6$Ge$_6$ has been claimed to be a possible candidate for kagomé metal with in-plane resistivity twice as large as the interplane resistivity. [23]. The unusual magnetic anisotropy was attributed to the presence of nearly flat bands slightly below Fermi level near the $\Gamma$ point toward the K and M points, which corresponds to the direction perpendicular to the z axis in real space. In addition to this, a dispersive band has been observed from $\Gamma$ to $\Lambda$, which corresponds to the direction along the z axis in real space (Fig S5a) [23]. Recent reports show the direct observation of the flat band associated with the $d_{x^2-y^2}$ orbital of the Cr atoms by angle-resolved photoemission spectroscopy (ARPES) [24]. We observed similar partially flat bands in LuFe$_6$Ge$_6$ running from $M$ to $\Gamma$ and from $\Gamma$ to A perpendicular and parallel to z axis respectively (Fig. S5b). The dispersive band running from $L$ to $A$ is also found to be present in LuFe$_6$Ge$_6$ just above the Fermi level, making it a potential host for interesting physical properties. The major difference in the character of these two bands seems to the orbital contribution, from density of states calculations the flat bands in LuFe$_6$Ge$_6$ seem to be associated with in plane $d_{x^2-y^2}$ orbitals instead of $d_{z^2}$. One interesting feature of these compounds is that the flat bands are dominated by the 3$d$ orbitals of the transition metals (Cr and Fe). No such flat bands near the Fermi level were observed in MgCo$_6$Ge$_6$, explaining the normal metallic resistivity we observe. A Dirac-type dispersion below the Fermi level relating to the direction perpendicular to z-axis in real space from the L to H points was observed in the band structure of MgCo$_6$Ge$_6$ (Fig S5c). The partial disorder in the Mg and Ge3 atoms could not be accounted for in the band structure calculations. However, the density of states calculation show that the bands near the Fermi level are not influenced by these atoms, making it likely that the disorder has little effect on the electronic structure near the Fermi level. DFT calculations show that hole doping of the MgCo$_6$Ge$_6$ system is expected to further move the band crossing near the Fermi level (Fig S5d, See SI Fig S4 for overlapping MgCo$_6$Ge$_6$ and LiCo$_6$Ge$_6$ band structure plots). ARPES combined with transport measurements will be helpful to shed more light on the role of the experimental band structures of these hexagonal lattice systems. Thus, obtaining large single crystals of these systems becomes crucial.
FIGURES:

Figure S1. (a) Heat capacity (C_p) divided by temperature cubed (T^3) versus log of temperature (T) for a single crystal piece of MgCo₆Ge₆, YCr₆Ge₆ and LuFe₆Ge₆. (b) Heat Capacity (Cp) divided by T² plot of a MgCo₆Ge₆ single crystal piece to extract the experimental Sommerfield coefficient (Ƴ) and β values using the equation C_p/T = Ƴ + βT² using the fit (red line) in the inset.

Figure S2. The Co kagomé lattice can be considered to be made up of rigid layers of alternate trimers shown in green and yellow. For the high temperature structure no tilt in the trimers was observed. The overall relaxation process can be understood in three steps. In step 1 the yellow trimers tilt in the anti-clockwise direction (by ~ 4.5°). Due to the rigid nature of these trimers the connecting Co atom at the atom relaxes tilting the green trimers in the clockwise direction by the same amount (Step 2). As a combination of these steps the internal angle of each Co hexagon deviates from 120° by ~ 9°. Similar tilting takes place in the opposite direction for the layer below (shown in blue) resulting in the final low temperature structure. As a consequence of this relaxation process the buckling of the Co layers occur in the a and b directions, evading the formation of a moiré superlattice.
Figure S3. Electronic band structure calculations of MgCo$_6$Ge$_6$ in $P6/mmm$ (dashed blue line) and $P6_3/mcm$ (black line) showing a dirac-type dispersion from the points L to H just below the Fermi level.

Figure S4. a) Electronic band structure calculations of MgCo$_6$Ge$_6$ (black line) in $P6/mmm$ which shows a Dirac-type dispersion (zoomed view in b) running from the points L to H just below the Fermi level. Hole doping of the system to LiCo$_6$Ge$_6$ (orange line) moves the band crossing near Fermi level, c) Brillouin zone for hexagonal lattice presented with special points and reciprocal lattice vectors.
Figure S5. a) Band structure of YCr$_6$Ge$_6$ showing the presence of linearly dispersed flat bands below Fermi level near the $\Gamma$ point toward the K and M points in addition to a dispersive band in the $\Gamma$-A direction. b) Similar flat bands observed in LuFe$_6$Ge$_6$ below the Fermi level in the M - $\Gamma$ and $\Gamma$ - A directions along with a Dirac dispersion from L-A just above the Fermi level. c) Electronic band structure calculations of MgCo$_6$Ge$_6$ in $P6_3/mmm$ which shows a Dirac-type dispersion running from the points L to H just below the Fermi level. d) Hole doping of the system to LiCo$_6$Ge$_6$ moves the band crossing near the Fermi level.
### Table S1. Crystallographic data for MgCo₆Ge₆ at T = 293(2) K.

| Crystal data          |            |
|-----------------------|------------|
| Chemical formula      | Co₆Ge₆Mg₀.₉ |
| M                     | 812.21     |
| Crystal system, space group | Hexagonal, P6/mmm |
| Temperature (K)       | 293        |
| a, c (Å)              | 5.06094 (15), 7.7271 (2) |
| V (Å³)                | 171.40 (1) |
| Z                     | 1          |
| Radiation type        | Mo Kα      |
| μ (mm⁻¹)              | 39.96      |
| Crystal size (mm)     | 0.08 × 0.06 × 0.01 |

| Data collection       |            |
|-----------------------|------------|
| Diffractometer        | SuperNova, Dual, Cu at zero, Atlas |
| Absorption correction | Analytical |
|                       | CrysAlis PRO 1.171.39.29c (Rigaku Oxford Diffraction, 2017) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| Tmin, Tmax            | 0.193, 0.692 |
| No. of measured, independent and observed [I > 2σ (I)] reflections | 4920, 170, 168 |
| Rint                  | 0.033      |
| (sin θ/λ)max (Å⁻¹)    | 0.766      |

| Refinement            |            |
|-----------------------|------------|
| R[F2 > 2σ (F2)], wR(F2), S | 0.013, 0.035, 1.26 |
| No. of reflections    | 170        |
| No. of parameters     | 19         |
| Δρmax, Δρmin (e Å⁻³)  | 1.11, -1.12 |

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### Table SII. Atomic coordinates obtained from structure solution to SXRD data at T = 293(2) K.

| Atoms | X   | Y   | Z    | Ueq  | Occupancy |
|-------|-----|-----|------|------|-----------|
| Ge1   | 2/3 | 1/3 | 0.0000 | 0.00623(17) | 1         |
| Ge2   | 2/3 | 1/3 | 0.5000 | 0.00732(17) | 1         |
| Ge3   | 0.0000 | 0.0000 | 0.16175(10) | 0.0087(2) | 0.945(5) |
| Mg    | 0.0000 | 0.0000 | 0.5000 | 0.0183(7) | 0.945(5) |
| Ge3'  | 0.0000 | 0.0000 | 0.302(7) | 0.055(5) | 0.055(5) |
| Co    | 0.5000 | 0.5000 | 0.25028(4) | 0.00962(17) | 1         |
| Atoms | $U_{11}$    | $U_{22}$    | $U_{33}$    | $U_{13}$    | $U_{12}$    | $U_{23}$    |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ge1   | 0.0071(2)   | 0.0071(2)   | 0.0045(3)   | 0.0000      | 0.0000      | 0.00354(10) |
| Ge2   | 0.0088(2)   | 0.0088(2)   | 0.0044(3)   | 0.0000      | 0.0000      | 0.00438(10) |
| Ge3   | 0.0076(2)   | 0.0076(2)   | 0.0110(4)   | 0.0000      | 0.0000      | 0.0096(5)   |
| Mg    | 0.0192(10)  | 0.0192(10)  | 0.0164(16)  | 0.0000      | 0.0000      | 0.0096(5)   |
| Ge3'  | 0.009(5)    | 0.009(5)    | 0.20(5)     | 0.0000      | 0.0000      | 0.005(2)    |
| Co    | 0.0144(2)   | 0.0144(2)   | 0.0067(2)   | 0.0000      | 0.0000      | 0.01227(19) |

**Table SIII.** Crystallographic data for MgCo$_6$Ge$_6$ at $T = 100(2)$ K.

| **MgCo$_6$Ge$_6$** |            |
|---------------------|------------|
| Crystal data        |            |
| Chemical formula    | Co$_6$Ge$_6$Mg$_{0.9}$ |
| $M$                 | 813.43     |
| Crystal system, space group | Hexagonal, $P6_3/mcm$ |
| Temperature (K)     | 100        |
| $a$, $c$ (Å)        | 5.05760(10), 15.4214(5) |
| $V$ (Å$^3$)         | 341.62(15) |
| $Z$                 | 2          |
| Radiation type      | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$)   | 40.089     |
| Crystal size (mm)   | 0.058×0.044×0.022 |

| Data collection     |            |
| Diffractometer      | SuperNova, Dual, Cu at zero, Atlas |
| Absorption correction| Analytical CrysAlis PRO 1.171.39.29c (Rigaku Oxford Diffraction, 2017) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| $T_{\text{min}}, T_{\text{max}}$ | 0.223, 0.513 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8533, 261, 248 |
| $R_{\text{int}}$    | 0.0377     |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.766 |

| Refinement          |            |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.0138, 0.0373, 1.221 |
| No. of reflections  | 261        |
| No. of parameters   | 21         |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å$^{-3}$) | 1.996, -0.976 |
**Table SIV.** Atomic coordinates obtained from structure solution to SXRD data at $T = 100(2)$ K.

| Atoms | $X$  | $Y$  | $Z$   | $U_{eq}$         | Occupancy |
|-------|------|------|-------|------------------|-----------|
| Ge1   | 2/3  | 1/3  | 0.2500| 0.00411(14)      | 1         |
| Ge2   | 1/3  | 2/3  | 0.5000| 0.00323(14)      | 1         |
| Ge3   | 0.0000| 0.0000| 0.08088(3)| 0.0044(2) | 0.905(6) |
| Mg    | 0.0000| 0.0000| 0.2500| 0.0090(5)       | 0.905(6) |
| Ge3'  | 0.0000| 0.0000| 0.1145(30)| 0.18(2)  | 0.095(6) |
| Co    | 0.0000| 0.52275(7) | 0.374(14)| 0.00394(14) | 1         |

| Atoms | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Ge1   | 0.0046(16) | 0.0046(16) | 0.00106(9) | 0.0000   | 0.0000   | 0.0039(1) |
| Ge2   | 0.0033(1)  | 0.0033(1)  | 0.00303(22)| 0.0000   | 0.0000   | 0.00167(8) |
| Ge3   | 0.0034(2)  | 0.0034(2)  | 0.0066(3)  | 0.0000   | 0.0000   | 0.0044(2) |
| Mg    | 0.0084(7)  | 0.0084(7)  | 0.0103(11)| 0.0000   | 0.0000   | 0.00905(53) |
| Ge3'  | 0.006(3)   | 0.006(3)   | 0.05(7)   | 0.0000   | 0.0000   | 0.018(2)  |
| Co    | 0.0021(1)  | 0.0048(1)  | 0.0042(2) | -0.0004(8)| 0.0000   | 0.00106(9) |

**Table SV.** Selected bond lengths (Å)

|          | $T = 293(2)$ K | $T = 100(2)$ K |
|----------|----------------|----------------|
| Ge3-Ge3  | 2.4997(16)     | 2.4946(10)     |
| Ge3-Mg   | 2.6137(8)      | 2.6081(5)      |
| Ge3-Co   | 6 x 2.6213(2)  | 3 x 2.5909(4), 3 x 2.7310(4) |
| Ge3’-Ge3’| 3.05(11)       | 3.06(11)       |
| Ge3’-Co  | 2.562(9)       | 3 x 2.419(3), 3 x 2.649(3) |
| Ge1-Co   | 2.4237(3) Å    | 2.4175(2)      |
| Ge2-Co   | 2.420(3) Å     | 2.4243(2)      |

**Table SVI.** Crystallographic data for YCr$_6$Ge$_6$.

|               | YCr$_6$Ge$_6$ |
|---------------|---------------|
| Crystal data  |               |
| Chemical formula | Cr$_6$Ge$_6$Y |
| $M$           | 836.45        |
| Crystal system, space group | Hexagonal, $P6/mmm$ |
| Temperature (K) | 100           |
\[ a, c (\text{Å}) \quad 5.15675 (18), 8.2679 (2) \]

\[ V (\text{Å}^3) \quad 190.41 (1) \]

\[ Z \quad 1 \]

Radiation type

Mo Kα

\[ \mu (\text{mm}^{-1}) \quad 38.90 \]

Crystal size (mm)

0.09 × 0.07 × 0.05

Data collection

Diffractometer

SuperNova, Dual, Cu at zero, Atlas

Absorption correction

Analytical

CrysAlis PRO 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

\[ T_{\text{min}}, T_{\text{max}} \quad 0.128, 0.284 \]

No. of measured, independent and observed \([I > 2\sigma (I)]\) reflections

4758, 186, 181

\[ R_{\text{int}} \quad 0.038 \]

\[ (\sin \theta/\lambda)_{\text{max}} (\text{Å}^{-1}) \quad 0.765 \]

Refinement

\[ R[F^2 > 2\sigma (F^2)], wR(F^2), S \quad 0.013, 0.031, 1.34 \]

No. of reflections

186

No. of parameters

15

\[ \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (\text{e Å}^{-3}) \quad 1.09, -0.86 \]

\textbf{Table SVII.} Atomic coordinates obtained from structure solution to SXRD data for YCr_{6}Ge_{6}.

| Atoms | X  | Y  | Z   | \(U_{eq}\)    | Occupancy |
|-------|----|----|-----|-------------|-----------|
| Ge1   | 2/3| 1/3| 0.0000 | 0.00320(15) | 1         |
| Ge2   | 2/3| 1/3| 0.5000 | 0.00280(15) | 1         |
| Ge3   | 0.0000 | 0.0000 | 0.15260(6) | 0.00309(16) | 1         |
| Y     | 0.0000 | 0.0000 | 0.5000 | 0.00346(18) | 1         |
| Cr    | 0.5000 | 0.5000 | 0.24939(5) | 0.00290(14) | 1         |

\textbf{Table SVIII.} Crystallographic data for LuFe_{6}Ge_{6}.

\begin{center}

\begin{tabular}{l|c|c|c|c|c}

\hline

\textbf{LuFe}_{6}\textbf{Ge}_{6} & \\

\hline

Crystal data & \\

Chemical formula & Fe_{6}Ge_{6}Lu & \\

\(M\) & 945.61 & \\

\hline

\end{tabular}

\end{center}
Crystal system, space group: Hexagonal, P6/mmm

Temperature (K) 100

\( a, c (\text{Å}) \) 5.09143 (12), 8.1002 (2)

\( V (\text{Å}^3) \) 181.85 (1)

\( Z \) 1

Radiation type: Mo K\( \alpha \)

\( \mu (\text{mm}^{-1}) \) 49.28

Crystal size (mm) 0.08 \times 0.06 \times 0.03

Data collection

Diffractometer: SuperNova, Dual, Cu at zero, Atlas

Absorption correction: Analytical CrysAlis PRO 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

\( T_{\text{min}}, T_{\text{max}} \) 0.104, 0.346

No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections: 5105, 180, 179

\( R_{\text{int}} \) 0.039

\( \sin(0/\lambdab)_{\text{max}} (\text{Å}^{-1}) \) 0.766

Refinement

\( R[F^2 > 2\sigma(F^2)], wR(F^2), S \) 0.013, 0.033, 1.27

No. of reflections 180

No. of parameters 15

\( \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (\text{e Å}^{-3}) \) 1.84, -0.84

Table SIX. Atomic coordinates obtained from structure solution to SXRD data for LuFe\( _6 \)Ge\( _6 \).

| Atoms | X   | Y   | Z     | U\( _{eq} \)         | Occupancy |
|-------|-----|-----|-------|----------------------|-----------|
| Ge1   | 2/3 | 1/3 | 0.0000 | 0.00326(17)          | 1         |
| Ge2   | 2/3 | 1/3 | 0.5000 | 0.00336(17)          | 1         |
| Ge3   | 0.0000 | 0.0000 | 0.15470(9) | 0.00252(16) | 1         |
| Lu    | 0.0000 | 0.0000 | 0.5000 | 0.00391(14)         | 1         |
| Fe    | 0.5000 | 0.5000 | 0.25098(6) | 0.00394(16) | 1         |
Table SX: Characteristic temperatures and number of oscillators of phonon modes obtained from the fit to the specific heat for single crystals of MgCo$_2$Ge$_6$, YCr$_3$Ge$_6$, and LuFe$_3$Ge$_6$.

| Mode   | T (K)  | Oscillator Strength (per formula unit) | Mode   | T (K)  | Oscillator Strength (per formula unit) | Mode   | T (K)  | Oscillator Strength (per formula unit) |
|--------|--------|----------------------------------------|--------|--------|----------------------------------------|--------|--------|----------------------------------------|
| Einstein | 121.4(4) | 1.56(2) | Debye | 363(1) | 11.44(2) | Debye | 336(1) | 12.8(1) | Debye | 591(26) | 4.1(1) |

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