Robust narrow-gap semiconducting behavior in square-net La₃Cd₂As₆

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ABSTRACT: Narrow-gap semiconductors are sought-after materials due to their potential for long-wavelength detectors, thermoelectrics, and more recently non-trivial topology. Here we report the synthesis and characterization of a new family of narrow-gap semiconductors, R₃Cd₂As₆ (R = La, Ce). Single crystal x-ray diffraction at room temperature reveals that the As square nets distort and Cd vacancies order in a monoclinic superstructure. A putative charge-density ordered state sets in at 279 K in La₃Cd₂As₆ and at 136 K in Ce₃Cd₂As₆ and is accompanied by a substantial increase in the electrical resistivity in both compounds. The resistivity of the La member increases by thirteen orders of magnitude on cooling, which points to a remarkably clean semiconducting ground state. Our results suggest that light square net materials within a I4/mmm parent structure are promising clean narrow-gap semiconductors.

I. INTRODUCTION

Electronic instabilities are ubiquitous in quantum materials. Notable examples include spin-density waves, superconductivity, and charge-density waves (CDWs). The latter is a modulation of conduction electron density accompanied by a periodic distortion of the crystal lattice.¹–³ Interestingly, CDWs have been recently observed in close proximity to exotic correlated phenomena, such as high-temperature superconductivity and axionic topological states.⁴–⁷

In addition, the formation of a CDW phase minimizes the energy of the system by opening a gap at the Fermi level, which may drive the material towards a narrow-gap semiconducting state.¹¹ Disorder-free narrow-gap semiconducting materials are of interest due to their potential functionalities, which include thermoelectricity, dark-matter detection, and nontrivial topology.⁸–¹⁰ Their narrow gap, however, often suffers from defects or impurities.¹¹,¹²

One way to design narrow-gap semiconductors is to search for low-dimensional crystal structures, which are fundamentally unstable to the formation of energy gaps from small distortions.¹³ In fact, CDW phases were initially identified in one-dimensional (1D) transition metal trichalcogenides MX₃ (M = Nb and Ta, X = S, Se, or Te) containing chains of NbSe₆ prisms and in quasi-2D layered transition metal dichalcogenides.¹³¹⁴

Here we consider layered tetragonal materials with the “112” general formula RMX₂ (R = lanthanide, M = Au, Ag, Cu, Cd, and Zn, X = Bi, Sb, and As), which contain pnictide square nets. Previous band structure analysis and molecular orbital models have shown that square nets built from more electronegative elements are prone to distortions that lift the tetragonal symmetry.¹⁵–¹⁷ This tendency occurs for two reasons. First, the R-square net p-bands close to the Fermi level (E_F) and the M d bands become well separated, which allows electron transfer and the formation of anionic units, that form covalent bonds leading to Zintl phases.¹³¹⁷ Second, there is greater mixing between s and p orbitals in pnictide elements with small atomic number (Z), which (again) favors the classic octet rule in a distorted structure over hypervalent bonds in an undistorted square net.¹³¹⁹

Important insights into distorted structures come from chalcogenide-based square nets, and numerous polytetrallurides host CDW phases with distorted Te square nets.
exhibit metallic behavior. Square net, rather than the partial or complete order-structure is argued to be a distortion in the tellurium portantly, the primary cause of the observed vacancy su-
to satisfy the Zintl rule in the distorted structure. Im-
In the latter, cation sites are partially occupied in order
 theoretically a rather underexplored phase space in which
conducting behavior in distorted arsenic square nets. We
room temperature, both compounds crystallize in a va-
crystalline powder was loaded along with iodine in a
K zone. The synthesized phase was investigated by Mo \( K_{\alpha} \)
single crystal x-ray diffraction and energy-dispersive x-
spectroscopy (EDX) both at room temperature. EDX
measurements confirmed the 3:2:6 stoichiometry within experimental error. The specific heat of a collection of approximately 10 single crystals (total mass \( \approx 1 \) mg) was measured using a Quantum Design PPMS that employs a quasi-adiabatic thermal relaxation technique. The electrical resistivity (\( \rho \)) was characterized with the same instrument in the standard four-probe configuration. The current was applied in the basal plane of the crystal. For \( \text{Ce}_3\text{Cd}_2\text{As}_6 \), an AC bridge was used to measure \( \rho \) in all temperature range. While, for \( \text{La}_3\text{Cd}_2\text{As}_6 \), \( \rho \) was measured with an AC bridge, at high temperatures, whereas at low temperatures a DC method was required due to the large resistance of the sample.

II. EXPERIMENTAL DETAILS

Black plate-like single crystals of \( \text{Ce}_3\text{Cd}_2\text{As}_6 \) and \( \text{La}_3\text{Cd}_2\text{As}_6 \) were grown by the vapor transport technique. First, a polycrystalline seed of \( 1\text{La}:0.7\text{Cd}:2\text{As} \) was prepared via solid state reaction at 800 °C. Then the polycrystalline powder was loaded along with iodine in a quartz tube, which was sealed in vacuum. The tube was kept in a temperature gradient from 830 °C to 720 °C for a week. The initial polycrystalline material was kept in the hot zone, and single crystals precipitated in the cold zone. The synthesized phase was investigated by Mo \( K_{\alpha} \) single crystal x-ray diffraction and energy-dispersive x-ray spectroscopy (EDX) both at room temperature. EDX measurements confirmed the 3:2:6 stoichiometry within experimental error. The specific heat of a collection of approximately 10 single crystals (total mass \( \approx 1 \) mg) was measured using a Quantum Design PPMS that employs a quasi-adiabatic thermal relaxation technique. The electrical resistivity (\( \rho \)) was characterized with the same instrument in the standard four-probe configuration. The current was applied in the basal plane of the crystal. For \( \text{Ce}_3\text{Cd}_2\text{As}_6 \), an AC bridge was used to measure \( \rho \) in all temperature range. While, for \( \text{La}_3\text{Cd}_2\text{As}_6 \), \( \rho \) was measured with an AC bridge, at high temperatures, whereas at low temperatures a DC method was required due to the large resistance of the sample.

III. RESULTS

We start with the structural characterization of \( \text{Ce}_3\text{Cd}_2\text{As}_6 \) and \( \text{La}_3\text{Cd}_2\text{As}_6 \). For both materials, Bragg reflections can be indexed in a tetragonal unit cell corresponding to the respective parent compounds with “112” stoichiometry. The approximate parameters of this \( 14/mmm \) structure are given in Table I. The corresponding tetragonal cell is shaded red in Fig. 1(a). A detailed summary of the refined parameters of either compound is provided in the Supporting Information. The occupancy of the Cd site (4d in \( 14/mmm \)) converges close
to 66% in both materials, confirming the stoichiometry measured in EDX.

Interestingly, the Cd vacancies are not randomly distributed, but rather order in a stripe pattern. Fig. 2 shows x-ray intensity maps interpolated to the (h,k,l) and (h0l) planes of reciprocal space (with reference to the I4/mmm cell). Aside from the integer-index Bragg peaks, a pattern of weak satellite reflections is observed, which is described by the propagation vector \( \mathbf{q}_{\text{Cd}} = \langle \frac{2}{3}, 0, \frac{2}{3} \rangle \). This indicates an ordering of the vacancies in a 3x1x3 superstructure [green cell in (a)], which can be reduced to a base-centered monoclinic structure of space group C2/m [blue cell in (a)].

Similar vacancy order has previously been observed in PrZn\(_{0.67}\)As\(_2\) (P4/nmm). In that case, the vacancy pattern also results in a stoichiometric “326” compound, but with orthorhombic (Pmmm) symmetry. By contrast, the vacancy stripes in Ce\(_3\)Cd\(_2\)As\(_6\) and La\(_3\)Cd\(_2\)As\(_6\) are staggered from one layer to the next in a sequence of six Cd layers. The transformation between the I4/mmm and C2/m cells, as illustrated in Fig. 2 is de-

### Table I: Structural parameters of R\(_3\)Cd\(_2\)As\(_6\), inferred from refinements in a tetragonal cell (neglecting superstructure reflections). A detailed summary of refined parameters and uncertainties for either compound (R = La, Ce) is provided in the Supporting Information.

| ion | Wyckl. | \(x\) | \(y\) | \(z\) | occ. (%) |
|-----|--------|-------|-------|------|---------|
| R   | 4e     | 0     | 0     | 0.11 | 100     |
| Cd  | 4d     | 0.1/2 | 1/4   | 0    | 66      |
| As1 | 4c     | 0.1/2 | 0     | 0    | 100     |
| As2 | 4e     | 0     | 0     | 0.34 | 100     |

### Table II: Description of R\(_3\)Cd\(_2\)As\(_6\) in the monoclinic setting. The parameters \( \alpha, \gamma, z, R \sim 0.11 \) and \( z_{\text{As}} \sim 0.34 \) refer to the I4/mmm parent cells, as stated in Table I. All sites are fully occupied. The refined \( x \) and \( z \) coordinates of the Wyckoff site 4i for either compound are given in the Supporting Information. The right column states the resulting approximate deviation (in \( \AA \)) with respect to the nominal positions in the monoclinic parent cell.

| R\(_3\)Cd\(_2\)As\(_6\), C2/m (\#12, unique axis b, cell choice 1) | nominal position | deviation (\( \AA \)) |
|---------------------------------------------------------------|-----------------|------------------|
| \( d = \alpha_t - \alpha_c \), i.e. \( d = \sqrt{a_t^2 + c_t^2} \sim 21.6 \AA \) | \( \beta = \gamma = 90^\circ \) | \( \beta = 90^\circ + \arctan(a_t/c_t) \sim 100.8^\circ \) |
| \( \bar{b} = -\bar{b}_t \), i.e. \( b = a_t \sim 4.1 \AA \) | \( \alpha = \gamma = 90^\circ \) | \( \alpha = \gamma = 90^\circ \) |
| \( \bar{c} = -3\bar{a}_t \), i.e. \( c = 3\alpha_t \sim 12.2 \AA \) | | |
| \( \alpha_t = \beta_t - \gamma_t \), i.e. \( \alpha_t = 3\alpha_t \sim 90^\circ \) | | |

FIG. 2. Comparison of experimental and calculated x-ray diffraction intensity maps of reciprocal space. The left and right halves of each panel show the measured and calculated intensity, respectively. For convenience, the data is indexed in the I4/mmm parent cell. (a,b) (hk\(\bar{z}\)) slices reveal the presence of (a) two stripe domains (i.e., twins) in LaCd\(_{0.67}\)As\(_2\) and (b) four in CeCd\(_{0.67}\)As\(_2\). (c,d) (h0l) slices show a large number of \( q_{\text{Cd}} = \langle \frac{2}{3}, 0, \frac{2}{3} \rangle \) superstructure peaks. The modulations of the intensities of these peaks is highly sensitive of small distortions of the ionic arrangement away from the nominal positions in the tetragonal parent.
The resulting staircase of Cd-vacancy stripes breaks the parent compounds’ fourfold symmetry, which is accompanied by several structural modifications. While the I4/mmm parent structure is determined by two ionic position parameters, twenty are required to define the C2/m counterpart (cf. Table I).

The satisfactory refinement within I4/mmm when superstructure reflections are ignored shows that these distortions are weak. Nonetheless, small deviations of these parameters away from their value in the I4/mmm setting cause significant variations of the structure factors of the superstructure peaks. This is illustrated in the reciprocal x-ray scattering intensity maps in Fig. 2. For comparison, each panel shows experimental intensities (left halves) along with our models (right halves). Details of this analysis are provided in the Supporting Information [11]. Major ionic displacements are summarized in Table I in terms of the deviations (dx and dz) relative to the ionic positions in the tetragonal parent compound. The full summary of refined parameters and uncertainties is given in the Supporting Information [11].

The refinement adequately captures that the Bragg intensities at (3/4l) are significantly weaker than those along (3/4l). This is due to a “relaxation” of Cd ions by about 0.25 Å towards the vacancy stripes, as illustrated in Fig. 2(c). As expected, the displacement of Cd ions also leads to a measurable displacement of their ligands (As1, As2 and As3), which causes a characteristic modulation of superstructure intensities along the l direction in reciprocal space.

Importantly, the arsenic square nets in the new “326” structure are also distorted. Here, the high-symmetry As1 site of I4/mmm splits into As4 – As7 (in C2/m). The As-As bond-lengths are then modulated by about 0.2 Å, as illustrated in Fig. 2(b), and become shorter along (3/4l). The tolerance factor defined by $t = d_{As-As}/d_{Ce/La-As}$ is no longer valid [13-19]. Whether the square-net distortion leads to Cd vacancies, similar to $K_{1/3}Ba_{2/3}AgTe_2$ in Ref. [22], or vice-versa remains an open question.

Finally, we note that no major structural differences have been observed between La$_3$Cd$_2$As$_6$ and Ce$_3$Cd$_2$As$_6$, aside from the expected lattice contraction from La to Ce, namely the volume of the Ce unit cell being smaller.

**FIG. 3.** (a) Electrical resistivity as a function of temperature for La$_3$Cd$_2$As$_6$. The inset shows the electrical resistivity of La$_3$Cd$_2$As$_6$ in the low temperature range. (b) Electrical resistivity as a function of temperature for Ce$_3$Cd$_2$As$_6$. Natural logarithm of the electrical resistivity as a function of 1000 over the temperature for La$_3$Cd$_2$As$_6$ (c) and for Ce$_3$Cd$_2$As$_6$ (d). The solid red lines are linear fits.
by 2.1%. Nonetheless, the La₃Cd₂As₆ crystal investigated featured only two of the four expected crystallographic twins corresponding to four propagation directions of the vacancy staircase, as observed in Ce₃Cd₂As₆ [Figs. 2(a,b)]. This observation could stem from extrinsic reasons, such as finite strain during crystal growth.

We turn to the physical properties of La₃Cd₂As₆ single crystals. Figures 3(a) and (b) display the in-plane electrical resistivity (ρ) of La₃Cd₂As₆ and Ce₃Cd₂As₆, respectively. Upon cooling, a sudden increase in the resistivity is observed at T_{CDW} = 279 K for La₃Cd₂As₆ and at T_{CDW} = 136 K for Ce₃Cd₂As₆. Below T_{CDW}, the observed semiconducting behavior indicates the opening of an energy gap due to the CDW phase transition, similar to Sr₃Ir₄Sn₁₂, Ca₃Ir₄Sn₁₂ and La₃Co₄Sn₁₃ [23,24]. Notably, the resistivity of La₃Cd₂As₆ increases up to 10¹⁰ Ω cm at 12 K, as presented in the inset of Fig. 3(a). This large increase of thirteen orders in magnitude is a rare property in narrow-gap semiconductors, which are typically prone to impurity bands that may dominate the electronic properties at low temperatures [25]. Remarkably, this increase was achieved in an as-grown single crystal, which suggests that sample quality could be improved through further purification. The broad hump around 50 K for Ce₃Cd₂As₆ may be associated with the depopulation of gap states [26], which may give rise to a superconducting state as in Sr₃Ir₄Sn₁₂ and La₃Co₄Sn₁₃ [23,24]. A negligible value of γ of 0.03(3) mJ/moK² and a Debye temperature (θ_D) of 291(2) K for La₃Cd₂As₆. Moreover, a negligible value of γ is expected in clean semiconducting compounds and confirms the high quality of La₃Cd₂As₆ single crystals.

The strong suppression of the CDW transition temperature and activation energy going from La₃Cd₂As₆ to Ce₃Cd₂As₆ is an indication that the application of external pressure may be an effective tuning parameter, given the volume unit cell contraction by about 2% in Ce₃Cd₂As₆ as compared to La₃Cd₂As₆. High pressure experiments are needed to investigate whether the CDW phases in La₃Cd₂As₆ and Ce₃Cd₂As₆ can be suppressed, which may give rise to a superconducting state as in Sr₃Ir₄Sn₁₂, Ca₃Ir₄Sn₁₂ and La₃Co₄Sn₁₃ [23,24]. Moreover, chemical pressure may also be an effective tuning parameter, and hence single crystals with smaller lanthanide el-
emments, such as Pr or Nd, are desirable. Finally, spectroscopic experiments are necessary to search for electronic instabilities, which could be driving the CDW phase in La₃Cd₂As₆ and Ce₃Cd₂As₆ and Ce₃Cd₂As₆, and the complete crystallographic information files for both compounds at room temperature.

IV. CONCLUSIONS

In summary, we report the structural and electrical transport properties of narrow-gap semiconductors Ce₃Cd₂As₆ and La₃Cd₂As₆, which crystallize in a distorted variant of the I₄/mmm tetragonal structure RCD₄/₃As₂. The resulting base-centered monoclinic superstructure with C2/m symmetry displays ordered Cd vacancies in a stripe pattern and a distorted As square net. Notably, both compounds feature charge density wave phases below 136 K (Ce₃Cd₂As₆) and 279 K (La₃Cd₂As₆), which suggests further distortion in the As square net. The CDW phases in these materials create gaps with estimated values of 105(1) meV and 74(1) meV for La₃Cd₂As₆ and Ce₃Cd₂As₆. A remarkable increase of thirteen orders of magnitude in the electrical resistivity was found for La₃Cd₂As₆ upon cooling from room temperature to 12 K. Coupled to the vanishingly small specific heat Sommerfeld coefficient, this result not only points to a robust semiconducting ground state in this class of compounds but also provides a route to realize clean narrow-gap semiconductors in distorted arsenic square net materials.

V. SUPPORTING INFORMATION

The Supporting Information consists of tables summarizing the crystallographic structure data for La₃Cd₂As₆ and Ce₃Cd₂As₆.

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REFERENCES

[1] Monceau, P. Electronic crystals: an experimental overview. Adv. Phys. 61 325 (2012).
[2] Grüner, G. The dynamics of charge-density waves. Rev. Mod. Phys. 60, 1129 (1988).
[3] Wilson, J. A.; Di Salvo, F. J.; Mahajan, S. Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides. Advances in Physics 24:2 117-201 (1975).
[4] Chen, C.-W.; Choe, J.; Morosan, E. Charge density waves in strongly correlated electron systems. Rep. Prog. Phys. 79 084505.
[5] Loret, B.; Auveray, N.; Gallais, Y.; Cazayous, M.; Forget, A.; Colson, D.; Julien, M.-H.; Paul, I.; Civelli, M.; Sacuto, A.; Intimate link between charge density wave, pseudogap and superconducting energy scales in cuprates. Nat. Phys. 15 771-775 (2019).
[6] Gooth, J.; Bradlyn, B.; Honnali, S.; Schindler, C.; Kumar, N.; Noky, J.; Qi, Y.; Shekhar, C.; Sun, Y.; Wang, Z.; Bernevig, B. A.; Felser, C. Axionic charge-density wave in the Weyl semimetal (TaSe₄)₂I. Nature 575 315-319 (2019).
[7] Shi, W.; Wieder, B. J.; Meyerheim, H. L.; Sun, Y.; Zhang, Y.; Li, Y.; Shen, L.; Qi, Y.; Yang, L.; Jena, J.; Werner, P.; Koepernik, K.; Parkin, S.; Chen, Y.; Felser, C.; Bernevig, B. A.; Wang, Z. A charge-density-wave topological semimetal. Nature Phys. 17:45-2481 (2021).
[8] Tomczak, J. M. Thermoelectricity in correlated narrow-gap semiconductors. J. Phys.: Condens. Matter 30 183001 (2018).
[9] Hochberg, Y.; Kahn, Y.; Lisanti, M.; Zurek, K. M.; Grushin, A. G.; Ilan, R.; Griffin, S. M.; Liu, Z.-F.; Weber, S. F.; Neaton, J. B. Detection of sub-MeV dark matter with three-dimensional Dirac materials. Physical Review D 97 015004 (2018).
[10] Xiao, Y.; Wang, D.; Qin, B.; Wang, J.; Wang, G.; Zhao, L.-D. Approaching Topological Insulating States Leads to High Thermoelectric Performance in n-Type PbTe. J. Am. Chem. Soc. 140 13097-13102 (2018).
[11] Shklovskii, Boris I.; Efros, Alex L. Electronic Properties of Doped Semiconductors; 1st Edition, Springer, Berlin,
bient and high pressures. Phys. Rev. B 46 8067 (1992).
I. ANALYSIS OF X-RAY DIFFRACTION DATA

By considering the structure factor of the 3 × 1 × 3 tetragonal supercell discussed in the manuscript, it can be shown analytically that the C/2m structure is the only vacancy pattern compatible with the superstructure reflection pattern observed in the (h,0,l) plane. The space group describing this atomic arrangement was identified using the FINDSYM algorithm of the ISOTROPY software suite\(^1,2\). A more quantitative analysis of the observed intensities was achieved as follows.

The Rigaku CrysAlisPro package was used to search the detector images for Bragg peaks and index them\(^3\). For both compounds (La\(_3\)Cd\(_2\)As\(_6\) and Ce\(_3\)Cd\(_2\)As\(_6\)), a close to complete (> 98\%) indexation of all observed peaks was achieved in the C/2/m cell (a \(\sim\) 21.6, b \(\sim\) 4.1, c \(\sim\) 12.2, \(\beta\) \(\sim\) 100.8°). Two (La) and four (Ce) crystallographic twins were taken into account, respectively. The intensities were integrated, and reprocessed for twinning, as implemented in CrysAlisPro.

The structures where solved using the Superflip charge flipping\(^4\) and EDMA\(^5\) Fourier peak search approach as implemented in Jana2006\(^6,7\). The algorithm reproducibly converged to the atomic arrangement presented in the manuscript. The position parameters of the 4\(i\) Wyckoff positions in C2/m were then refined using Jana2006 and are summarized below in Tables III and IV. The quality of the refinement is limited by the strong overlap of weak superstructure intensities that have to be assigned to multiple twins.
II. PSEUDO-TETRAGONAL STRUCTURES

Tables I and II show the refinement results of LaCd$_{2/3}$As$_2$ and CeCd$_{2/3}$As$_2$ XRD datasets when treated as non-stoichiometric tetragonal compounds (with ~33% disordered Cd vacancies), i.e. ignoring any superstructure reflections. Given that we have demonstrated the breaking of the 4-fold symmetry in these crystals, Tables I and II should not be perceived as correct crystallographic data but merely represent hypothetical compounds. The purpose of these refinements is to estimate the positions of La/Ce and As$_2$ ions along the z-axis. We use this information to infer the atomic displacements d$x$ and d$z$ (cf. Tables III and IV) relative to these (hypothetical) tetragonal compounds.

The comparison of goodness-of-fit and residual ($R$) values between the $I4/mmm$ and $C2/m$ refinements also provides some guidance to the level of improvement of the refinement quality by taking into account the true symmetry of the materials. These parameters are defined as

$$R(F) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad \text{for } F_o^2 > 2\sigma(F_o^2)$$

$$R_w(F_o^2) = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2},$$

where $F_o$ and $F_c$ are the observed and calculated structure factors.

| LaCd$_{2/3}$As$_2$ | CeCd$_{2/3}$As$_2$ |
|-------------------|-------------------|
| Formula mass (g/mol) | 364.1             | 365.3             |
| Temperature (K)    | 293               | 293               |
| Crystal System     | tetragonal        | tetragonal        |
| Space Group        | $I4/mmm$ (#139)   | $I4/mmm$ (#139)   |
| f.u./cell (Z)      | 4                 | 4                 |
| $a$ (Å)            | 4.1030(6)         | 4.0709(6)         |
| $b$ (Å)            | 4.1030(5)         | 4.0709(4)         |
| $c$ (Å)            | 21.356(3)         | 21.227(3)         |
| $\alpha$ (°)      | 90.000(11)        | 90.000(9)         |
| $\beta$ (°)       | 90.000(12)        | 90.000(11)        |
| $\gamma$ (°)      | 90.000(12)        | 90.000(10)        |
| $V$ (Å$^3$)        | 359.52(9)         | 351.78(8)         |
| $\rho_{calc}$ (g/cm$^3$) | 6.7261             | 6.8971             |
| $F$ (000)          | 614               | 624               |
| $2\theta$ (°)     | 1.91 - 29.39      | 1.92 - 29.00      |
| Crystal Size ($\mu$m$^3$) | 25 × 20 × 15     | 25 × 20 × 15     |
| Radiation          | Mo K$_\alpha$    | Mo K$_\alpha$    |
| Wavelength (Å)     | 0.71              | 0.71              |
| $\mu$ (mm$^{-1}$)  | 33.723            | 35.261            |
| Number of reflections | 177              | 174              |
| Parameters         | 9                 | 8                 |
| Structure factor coefficient | $|F|$            | $|F|$            |
| Goodness of fit    | 5.30              | 4.94              |
| $R(F)$ (%)         | 10.33             | 9.60              |
| $R_w(F_o^2)$ (%)   | 12.27             | 10.53             |

| Ce        | 4e | 0   | 0   | 0.1087(1) | 0.004(1) | 100 |
|------------|----|-----|-----|-----------|----------|-----|
| Cd         | 4d | 0   | 1/2 | 1/4       | 0.030(3) | 63(2)|
| As1        | 4c | 0   | 1/2 | 0         | 0.022(2) | 100 |
| As2        | 4e | 0   | 0   | 0.3351(3) | 0.011(2) | 100 |

TABLE I. Structural refinement of LaCd$_{2/3}$As$_2$ as a hypothetical tetragonal compound with Cd vacancies.

| Ce        | 4e | 0   | 0   | 0.1087(1) | 0.004(1) | 100 |
|------------|----|-----|-----|-----------|----------|-----|
| Cd         | 4d | 0   | 1/2 | 1/4       | 0.027(3) | 62(2)|
| As1        | 4c | 0   | 1/2 | 0         | 0.013(1) | 100 |
| As2        | 4e | 0   | 0   | 0.3365(2) | 0.006(1) | 100 |

TABLE II. Structural refinement of CeCd$_{2/3}$As$_2$ as a hypothetical tetragonal compound with Cd vacancies.
### III. Refined Monoclinic (C2/m) Structures

Tables III and IV summarize the refinements of the same XRD datasets (as in Tables I and II) in the monoclinic $C2/m$ cell. This is the correct description, corresponding to stoichiometric “326” compounds. Aside from refined atomic position data, we list the resulting deviations $dx$ and $dz$ in (Å units) from the nominal atomic positions in the respective tetragonal cells, as inferred from Tables I and II. Deviations larger than 0.1 Å are highlighted in red font. The transformation from the tetragonal to monoclinic atomic parameters is stated in Table II of the manuscript.

#### La$_3$Cd$_2$As$_6$

| atomic positions | deviations (Å) | dx | dz | U |
|------------------|----------------|----|----|---|
| La1 4i 0.10945(15) | 0 0.0374(7) | ±0 | +0.020 | 0.0040(10) |
| La2 4i 0.10965(15) | 0 0.7021(8) | +0.007 | −0.022 | 0.0040(10) |
| La3 4i 0.10897(16) | 0 0.3665(7) | −0.009 | −0.071 | 0.0040(10) |
| Cd1 4i 0.25135(20) | 0 0.8947(8) | +0.029 | −0.271 | 0.0103(7) |
| Cd2 4i 0.25130(19) | 0 0.6016(8) | +0.028 | +0.225 | 0.0103(7) |
| As1 4i 0.3328(3) | 0 0.1151(14) | −0.050 | −0.003 | 0.0101(6) |
| As2 4i 0.3399(3) | 0 0.7787(14) | +0.104 | +0.004 | 0.0101(6) |
| As3 4i 0.3332(3) | 0 0.4442(14) | −0.041 | −0.010 | 0.0101(6) |
| As4 2b 0 1/2 0 | 0 — — 0.0101(6) |
| As5 4i 0.0005(4) | 0 0.1770(5) | +0.011 | +0.127 | 0.0101(6) |
| As6 4i 0.5013(5) | 0 0.3488(5) | +0.028 | +0.191 | 0.0101(6) |
| As7 2c 0 0 1/2 | 0 — — 0.0101(6) |

**TABLE III.** Structural refinement of La$_3$Cd$_2$As$_6$.

#### Ce$_3$Cd$_2$As$_6$

| atomic positions | deviations (Å) | dx | dz | U |
|------------------|----------------|----|----|---|
| Ce1 4i 0.10901(12) | 0 0.0399(3) | +0.007 | +0.045 | 0.0067(9) |
| Ce2 4i 0.10917(12) | 0 0.7046(3) | +0.010 | +0.021 | 0.0065(9) |
| Ce3 4i 0.10831(12) | 0 0.3686(3) | −0.008 | −0.012 | 0.0056(8) |
| Cd1 4i 0.2516(2) | 0 0.8949(5) | +0.035 | −0.266 | 0.0124(5) |
| Cd2 4i 0.25162(2) | 0 0.6024(5) | +0.035 | +0.233 | 0.0124(5) |
| As1 4i 0.3343(2) | 0 0.1130(6) | −0.048 | +0.010 | 0.0081(1) |
| As2 4i 0.34176(19) | 0 0.7814(6) | +0.114 | +0.031 | 0.0052(1) |
| As3 4i 0.3340(2) | 0 0.4458(6) | −0.054 | +0.037 | 0.0081(1) |
| As4 2b 0 1/2 0 | 0 — — 0.081(1) |
| As5 4i 0.9990(3) | 0 0.1773(3) | −0.022 | +0.130 | 0.0081(1) |
| As6 4i 0.4992(4) | 0 0.3490(4) | +0.017 | +0.192 | 0.0081(1) |
| As7 2c 0 0 1/2 | 0 — — 0.0081(1) |

**TABLE IV.** Structural refinement of Ce$_3$Cd$_2$As$_6$. 

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REFERENCES

[1] Stokes, H. T.; Hatch, D. M. FINDSYM: program for identifying the space-group symmetry of a crystal, Journal of Applied Crystallography 38 237 (2005).
[2] Stokes, H. T.; Hatch, D. M.; Campbell, B. J. Fndsym, isotropy software suite, iso.byu.edu.
[3] Agilent Technologies, (2013), CrysAlisPro Software system, Agilent Technologies UK Ltd, Oxford, UK.
[4] Oszlányi, G.; Sütő, A. Ab initio structure solution by charge flipping. Acta Crystallographica Section A 60 134 (2004).
[5] Palatinus, L.; Prathapa, S. J.; van Smaalen, S. EDMA: a computer program for topological analysis of discrete electron densities. Journal of Applied Crystallography 45 575 (2012).
[6] Petřiček, V.; Dušek, M.; Palatinus, L. Crystallographic computing system jana2006: General features. Zeitschrift für Kristallographie - Crystalline Materials 229 345 (2014).
[7] Petřiček, V.; Dušek, M.; Plíšil, J. Crystallographic computing system jana2006: solution and refinement of twinned structures. Zeitschrift für Kristallographie - Crystalline Materials 231 582 (2016).