1. Introduction

The first superconductor whose detailed phenomenology could not be described by conventional BCS theory, CeCu$_2$Si$_2$, was reported by Steglich and coworkers three decades ago. CeCu$_2$Si$_2$ forms in the ‘122 type’ ThCr$_2$Si$_2$ crystal structure and superconducts below ~ 0.5 K [1]. This was unexpected, as it was found only four years after CeAl$_3$ was reported as the first heavy-fermion compound [2]. A very important class of heavy-fermion superconducting materials of current interest, the ‘115 superconductors’ CeMIn$_5$ (M = Co, Rh, Ir), was announced in 2001 [3]. The significance of the ‘Ce-115’ family originates from the unique opportunity it offers to explore the relationship between unconventional superconductivity and magnetism, and its study has resulted in more than a thousand papers published in the last decade. It has been shown that ‘Ce-115’ compounds belong to a more general A$_n$M$_m$In$_{3n+2m}$ family, where M is a group 9 transition metal and A is not only Ce but can also be U, Np or Pu. Recently, it has been shown that extension to group 10 metals is possible, but only for a higher order members of the structural family, i.e. n = 2, m = 1 (Ce$_2$PdIn$_8$ [4–6]), n = 1, m = 2 (CePt$_2$In$_7$ [7]), n = 3, m = 1 (Ce$_3$PdIn$_{11}$ [8] and Ce$_3$PtIn$_{11}$ [9]). The current understanding of the heavy-fermion superconductivity in the A$_n$M$_m$In$_{3n+2m}$ family is discussed in [10].

The crystal structures for the four known members of A$_n$M$_m$In$_{3n+2m}$ family are presented in figure 1. The first member (CeIn$_3$) forms in a primitive cubic structure, and is a common building unit for the more complex A$_n$M$_m$In$_{3n+2m}$ compounds. The next two members, CeMIn$_5$ and Ce$_2$MIn$_8$, form in a primitive tetragonal structure (P4/mmm), whereas CePt$_2$In$_7$ crystallizes in a body-centred tetragonal structure (I4/mmm). These higher order members consist of CeIn$_3$ and MIn$_2$ blocks stacked along the c-axis. As can be seen
in figure 1, the largest ($c = 21.57 \text{Å}$) unit cell is observed for CePt$_2$In$_7$. The crystal structure of this compound was first described by Kurenbaeva et al [7] and later confirmed by Tobash et al [11]. Here, we show that that model is not correct, and present the correct model for the crystal structure of CePt$_2$In$_7$ (figure 1(d)), employed in the interpretation of NMR data on this compound [12]. Electronic structure calculations are performed based on this crystal structure, and the consequences of the differences in structure are described.

2. Experimental

Plate-like single crystals of CePt$_2$In$_7$ were grown from a high-temperature solution as described in [11]. The starting high purity (99.9% Pt, 99.9% Ce, 99.99% In) metals, in the ratio of Ce:Pt:In 1:3:20, were placed in an alumina crucible and sealed under vacuum in a quartz tube. The tube was heated to 1180 °C and kept at that temperature for 8 h, and then cooled to 800 °C over a period of 1–1.5 h, followed by slow cooling to 400 °C at the rate of 4 °C/h. Excess In was spun off at 400 °C with the aid of a centrifuge.

Single crystal XRD measurements were performed using a Bruker APEX II Quazar diffractometer with monochromated Mo $K\alpha$ irradiation collecting four spheres of data in the 0 range from 3.78 to 38.54°. Frames were collected with an irradiation time of 4 s per frame and combined $\omega$- and $\varphi$- scan technique with $\Delta\omega = \Delta\varphi = 0.5^\circ$. Data were corrected to Lorentz and polarization effects, and an experimental adsorption correction with SADABS [13] was applied. The structures were solved by direct methods and refined to an optimum R1 value with SHELX-2013 [14].

The electronic structure calculations were performed in the framework of density functional theory (DFT) using the WIEN2K code with a full-potential linearized augmented plane-wave and local orbitals [FP-LAPW+lo] basis [15] together with the Perdew–Burke–Ernzerhof (PBE) parametrization [16] of the generalized gradient approximation (GGA) as the exchange-correlation functional. The plane-wave cutoff parameter RKMAX was set to 8 and the Brillouin zone was sampled by 10,000 $k$ points. The results of calculations that do not include spin–orbit coupling (SOC) are presented. The inclusion of SOC did not significantly change the calculated total energy for the different structural models.

3. Results

Single crystal x-ray diffraction patterns were collected at a temperature of 173 K. The structure was solved using direct methods on $F^2$. Three structural models were tested (table 1) and the refined lattice parameters are the same for all models. They are approximately 0.2% larger and smaller than those reported in [7] and [11], respectively. For the first two (A and B), the atoms have the same positional coordinates but the occupations of the sites are taken as variable (see table 2). Model A assumes 100% site occupation and has no atom admixture present, i.e. it has no structural
disorder. This model, a fully ordered variant of the previously reported structure, is certainly not correct as it returns a negative thermal parameter (Ueq) for the In1 position, a large thermal parameter for the Ce position and an unacceptable goodness of fit value (GOF = 2.143). Model B has the same atomic positions as Model A and is based on the crystal structure reported in [7] and confirmed in [11]. This model assumes partial Ce site occupancy (85%), and, in addition, that the In1 site is an admixture of In and Pt in the ratio 75:25. The refinements of model B give a much lower GOF = 1.089. However, as the authors of [11] pointed out, the presence of a large number of Ce site vacancies, and the strong structural disorder due to Pt/In site mixing is in contradiction to the observed very low residual resistivity (\(\rho_0 = 0.2\ \mu\Omega\ cm\)) and very high residual resistivity ratio (RRR = 400) observed for this material.

We have corrected this structural model by replacing the Indium in the Wyckoff 2b position by Cerium. The removed indium is then placed in the Wyckoff 2a position (see table 2), maintaining the material stoichiometry. The structure has 100% site occupancies and no structural disorder. The quality of the refinement is excellent. The GOF obtained is 1.022, and the residual electron densities are excellent. This structure, with no structural disorder, as opposed to the former one, resolves the discrepancy between the transport properties and crystal structure of the compound.

In the new crystal structure (figure 1(d)), the stacking of the Pt–In blocks is changed relative to the previously reported model. The most important consequence of this difference is a much shorter Ce–Pt distance. The inset of figure 1 presents the local coordination environment of a Ce atom (green ball), inside a polyhedron formed by In atoms (purple balls). The corrected model places the Pt in a position where it caps the Ce–In polyhedra giving a much shorter Ce–Pt distance. The inset of figure 1 presents the local coordination environment of a Ce atom (green ball), inside a polyhedron formed by In atoms (purple balls). The correct placement of Pt in this position is in very good agreement with d_{Ce-Pt} observed for all other Ce-based CeM_{m}In_{3m+2n} compounds, an additional indication of its correctness.

| Table 2. | Atomic coordinates and equivalent isotropic displacement parameters (pm^2 × 10^{-3}) for each model as described in the text. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. Structure model C is the correct structure for CePt_2In_7. |
|----------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| **Model A**   | **Model B [7, 11]**                          | **Model C (this work)**                        |
| Ce(1)         | 2a 0 0 0                                   | 2a 0 0 0                                     | 2b 0 0 0                                     |
| Pt(1)         | 4e 0 0 0.3256(1)                           | 4e 0 0 0.3256(1)                             | 4e 0 0 0.3256(1)                             |
| In(1)         | 2b 0 0 0.5                                 | 2b 0 0 0.5                                  | 2b 0 0 0.5                                  |
| In(2)         | 4d 0 0.5 0.25                              | 4d 0 0.5 0.25                               | 4d 0 0.5 0.25                               |
| In(3)         | 8g 0 0.5 0.1079(1)                         | 8g 0 0.5 0.1079(1)                          | 8g 0 0.5 0.1079(1)                          |
| **Model B [7, 11]** | **Model C (this work)**                        | **Model C (this work)**                        |
| Ce(1)         | 2a 0 0 0                                  | 2b 0 0 0.5                                 | 2b 0 0 0.5                                 |
| Pt(1)         | 4e 0 0 0.3256(1)                           | 4e 0 0 0.3256(1)                             | 4e 0 0 0.3256(1)                             |
| In(1)         | 2a 0 0 0.5                                | 2a 0 0 0.5                                 | 2a 0 0 0.5                                 |
| In(2)         | 4d 0 0.5 0.25                             | 4d 0 0.5 0.25                              | 4d 0 0.5 0.25                              |
| In(3)         | 8g 0 0.5 0.1079(1)                        | 8g 0 0.5 0.1079(1)                         | 8g 0 0.5 0.1079(1)                         |
Figure 2 shows the calculated density of states (DOS) for the ordered models: former (A) and correct (C). The density of states for the highly disordered model (B) cannot reliably be calculated by the DFT method at the present time. The DOS at the Fermi level is similar, but with 2 eV above and below the Fermi level there are significant differences, for example the presence of a small shoulder slightly above the Fermi level that is due to Ce-f states. Despite a similar DOS, the Fermi surfaces derived from the structures are quite different, as is shown in figure 3. For both structures, there are four bands crossing the Fermi level. For the former model (A), there are three cylinders at the edges of the Brillouin zone with little k_z dispersion, together with a more delocalized band that also shows little dispersion in the k_z direction; this can be attributed to the more 2D character of the structure of model A. The calculated Fermi surface is in agreement with that reported in [17]. For the correct model (C), there are only two bands at the Brillouin zone boundary, one with cylindrical symmetry and one with more rectangular symmetry. Both bands have 2D character; however, both are slightly warped. One of the four bands is almost fully occupied and only provides small pockets around the zone boundary.

Figure 2. Density of states per formula unit for both structural models. Model (A) ordered version of former model, Model (C) the correct model. Inset: the Fermi-surface for the correct model.

Figure 3. Comparison of the Fermi surfaces of the two models. The first Brillouin zone is drawn in black. In both cases, four bands cross the Fermi level. In the former model (A), there are three cylinders with little dispersion in the z-direction, whereas the Fermi surface becomes more 3D in the correct model (C) with only two 2D Fermi surfaces. One of the bands in the correct model is almost fully occupied and provides only barely visible small pockets and the zone boundary.

Figure 4 shows the introduction of spin–orbit coupling (SOC) into the calculation does not influence the states at the Fermi level, as is shown in figure 4. The Ce-f states are split with a large peak in the DOS approximately 0.2 eV above the Fermi level. This 4f-peak is also observed in CeRhIn5, where it coincides with the Fermi level [17].
4. Conclusions

Knowledge of the crystal structure of a material with interesting physical properties is critical for its understanding. The structural parameters are, for example, required as the input for electronic structure calculations and, from the experimental point of view, the knowledge of atomic positions in the unit cell is critical for analysis of NMR/NQR results and quantum oscillation measurements that characterize the electronic band structure. Here, we have reported a corrected structural model for CePt2In7, with different Pt–In stacking, that has a similar statistical agreement to the observed diffraction intensities as the previously reported model [11]. However, the absence of the significant number of Ce site vacancies, and strong Pt–In site disorder is much more consistent with reported physical properties. In addition, the Ce–Pt local coordination is much more consistent with that of the other members of the structural family. The density of states calculation reveals important differences between the two crystal structures. Instead of four 2D bands at the Fermi level, calculations performed for the corrected structure reveal three bands that are more 3D. These result from the fact that in the corrected crystal structure, the Ce–Pt distance is shorter, which allows for Ce–Pt electronic interactions and increases the electronic dimensionality. Finally, our DOS calculations show that the new structural model for CePt2In7 has a significantly lower energy than the one reported earlier.

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Figure 4. Density of states for the correct structural model (C) with spin–orbit coupling included. The DOS at the Fermi level is barely changed, as is the Fermi surface. The Ce-f states are heavily influenced by spin–orbit coupling.